# Cluster model studies on the electronic and magnetic properties of LaCo$_{13}$ and La(Fe$_x$Al$_{1-x}$)$_{13}$ alloys

G. W. Zhang, X. G. Gong,[a] and Q. Q. Zheng[a),b)]
*Institute of Solid State Physics, Academia Sinica, 230031 Hefei, People's Republic of China*

J. G. Zhao
*Institute of Physics, Academia Sinica, 100080 Beijing, People's Republic of China*

We present studies on both the electronic and magnetic properties of LaCo$_{13}$ and La(Fe$_x$Al$_{1-x}$)$_{13}$ intermetallic compounds by cluster model calculations within the scheme of density-functional theory. The equilibrium structures of the isolated and embedded clusters, obtained by minimizing the total binding energy, are in good agreement with available experimental data and other theoretical results. The relative stability and formation of LaCo$_{13}$ and La(Fe$_x$Al$_{1-x}$)$_{13}$ phases have been successfully explained. Interesting changes of magnetic properties in an Al doped Fe$_{13}$ cluster have been obtained. The possible effect of Al on the magnetic phase diagram of La(Fe$_x$Al$_{1-x}$)$_{13}$ is discussed.

The cubic NaZn$_{13}$-type alloys have long been the subject of much research. Recently, the successful fabrication of LaCo$_{13}$, La(Fe$_x$Al$_{1-x}$)$_{13}$ alloys have enriched this family and attracted much experimental and theoretical interest.[1] Their structures are based on a faced-centered cubic lattice with the space group $O_{h6}$–F$_{m3c}$ and eight molecular formulas in the unit cell. La atoms (e.g., for LaCo$_{13}$) are at the body centered positions. There are two nonequivalent positions for Co atoms. One of the important features of this structure is that Co$_I$ is surrounded by 12 Co$_{II}$ at the vertices of a regular icosahedron, and the La atom is at the center of a snub cube, with Co$_{II}$ atoms at its 24 vertexes. It is well known that the icosahedral structures are very stable for many kinds of 13-atom clusters. The relative stability and electronic structure of the local icosahedral cluster may contribute to the formation of the characteristic NaZn$_{13}$-type structure. In experiments, it has been found that LaCo$_{13}$ alloy is stable, while the LaFe$_{13}$ alloys is not stable, but it can be stabilized by suitable doping with Al atoms. Many experiments show that La(Fe$_x$Al$_{1-x}$)$_{13}$ alloys are only stable with the $x$ range between 0.46 and 0.92.[2] Neutron diffraction experiments suggest that Fe and Al atoms not be randomly distributed in the alloys, the Co$_I$ sites be completely occupied by Fe, Al atoms substitute Fe atoms in the Co$_{II}$ sites.[3] The doping of Al in the icosahedral Fe$_{13}$ cluster changes both relative stability and electronic structures of the local unit structure, which consequently favors the formation of NaZn$_{13}$-type alloys. The doping of Al also changes the magnetic properties of La–Fe alloys. The measurement of susceptibility reveals that La(Fe$_x$Al$_{1-x}$)$_{13}$ alloys exhibit a unique magnetic diagram varying from the micromagnetic state to the ferromagnetic state and the antiferromagnetic state, with the increase of the Fe concentrations. The measurement of electrical resistivity and magnetization also suggest that local electronic and magnetic properties have played an important role in properties of those alloys.[4] It is natural to ask why LaCo$_{13}$ alloys are stable, while LaFe$_{13}$ is only stable with some doping of Al, and also why the variant doping changes the magnetic and electronic properties? These problems are not been fully understood. In this paper, based on a cluster model, we have calculated the electronic structures and the total binding energies of LaCo$_{13}$ and La(Fe$_x$Al$_{1-x}$)$_{13}$ alloys, trying to understand the relative stability of these alloys from a local structure point of view, and identify the role played by Al atoms in the La(Fe$_x$Al$_{1-x}$)$_{13}$ alloys. We have used the icosahedral Co$_{13}$, Fe$_{13}$, and Fe$_{12}$Al clusters to study the local properties of LaCo$_{13}$ and La(Fe$_x$Al$_{1-x}$)$_{13}$ alloys. To take into account the effects of the crystal field, we also have studied the clusters embedded in the crystal. The calculations are performed using the density functional theory with a local spin density approximation.[5] The discrete variational method has been used to solve the Kohn–Sham equation.[6] In our calculations, the basis sets are the numerical atomic valence orbitals of $3d4s$ for Fe and Co atoms, and $3s3p$ for the Al atom, we have found that when including the more diffusive orbitals in the basis set, there were very small effects on equilibrium atomic distances and electronic structures. The inner orbitals are kept frozen in all the calculations. Group theory has been adopted to classify the molecular orbitals and consequently simplify the calculations. The equilibrium structures of all the calculated clusters are obtained by minimizing the total binding energies for several center to vertex distances, keeping the corresponding symmetry. The binding energy is defined by $E_b = E_{tot} - E_{ref}$, where $E_{tot}$ is the total energy of the cluster and $E_{ref}$ is the sum of the total energies of individual atoms. We have used the Mulliken population to get the occupation numbers for atomic orbitals.[7] The magnetic moments for each atom are the difference of electrons between spin-up and spin-down states.

In Table I, we have presented the calculated magnetic moments and the theoretical equilibrium distances from center to vertex for Co$_{13}$, Fe$_{13}$, and Fe$_{12}$Al clusters, but for the embedded clusters, we have used the experimental atomic distances in the corresponding bulk phases. From Table I, we can see that the equilibrium distances of Co$_{13}$ and Fe$_{13}$ are almost the same, the small difference may come from the difference of atomic sizes for Co and Fe atoms. Actually, the

---

TABLE I. Some properties of all the calculated clusters. $\mu_c$ is the magnetic moments of $Co_I$ sites. $\mu$ is the average magnetic moments per the Fe or Co atom of a cluster.

| | Isolated clusters | | | Embedded clusters | | |
|---|---|---|---|---|---|---|
| | $Co_{13}$ | $Fe_{13}$ | $Fe_{12}Al$ | $Co_{13}$ | $Fe_{13}$ | $Fe_{12}Al$ |
| $d_0$ (a.u.) | 4.65 | 4.63 | 4.73 | 4.64 | 4.57 | 4.59 |
| $\mu_c(\mu_B)$ | 2.38 | 3.25 | 2.97 | 2.94 | 3.85 | 4.20 |
| $\mu(\mu_B)$ | 2.38 | 3.38 | 2.99 | 2.83 | 3.83 | 4.20 |

atomic size effects on the lattice constants can also be observed in $LaCo_{13}$ and $LaFe_{13}$ alloys, the distance between $Co_I$ and $Co_{II}$ in $LaCo_{13}$ is 4.64 a.u., similarly, the distance between $Fe_I$ and $Fe_{II}$ in $LaFe_{13}$ extrapolated from experimental data[2] is 4.57 a.u. The fact that the theoretical equilibrium distance for the icosahedral $Co_{13}$ and $Fe_{13}$ are very close to the experimental value in the $LaM_{13}$ (M=Co,Fe) bulk phases suggest that the local icosahedral cluster will not be affected very much by the crystal environments. When substituting Fe with Al, we found an increase of equilibrium distance, which is in agreement with the experimental fact that the lattice constant increases with the increase of Al concentrations. This phenomenon can be easily understood, because the Al atoms have more diffusive electronic orbitals and hence a large atomic size. In Fig. 1, we show the calculated binding energies for all the clusters at the equilibrium center to vertex distance $d_0$. We obtained about ~45 eV binding energy for the $Fe_{13}$ cluster, which is also in agreement with other theoretical calculations,[8] and the $Co_{13}$ has about ~30 eV binding energy. On doping Al in the $Fe_{13}$, as shown in the figure, we found the binding energy of $Fe_{12}Al$ shifted up a little bit. We can expect that the binding energy will increase if the shifting Al atom outward deviated from a perfect icosahedron. In Fig. 2, we have plotted the eigenvalue spectra for all the calculated clusters. In the $Co_{13}$ clus-

ter, we obtained a fourfold degenerate $G_g$ molecular orbital for the highest occupied state (HOMO), but the HOMO is not completely occupied and there are three electron deficiencies, so, in principle, the isolated icosahedral $Co_{13}$ will not be stable, at least Jahn–Teller distortion will lower the total energy. But why are the $LaCo_{13}$ alloys with an icosahedral structural unit stable? This striking question can probably be understood as following. It is well known that the La atom has a strong tendency to lose three valence electrons. If La atom support $Co_{13}$ with three electrons to fill the deficiency in HOMO, it makes the icosahedral $Co_{13}$ stable with a closed electron shell. The large ion core of La atoms fills the space among icosahedral $Co_{13}$ clusters. In this way, the icosahedral $Co_{13}$ can be considered as superatoms, the complicated $LaCo_{13}$ alloys can be composed of a *superatom* $Co_{13}$ and La atom. In fact, the idea of superatom that had been used successfully to explain the stability of icosahedral quasicrystals[9] is also applicable to many other systems. We have checked other Zn based $AB_{13}$ alloys, we found the same explanation can be used. In the similar way, we can understand the stability of $LaFe_{13}$ alloys. In the $Fe_{13}$ cluster, we obtain a five-fold degenerate $H_g$ molecular orbital for the HOMO, but with only one electron in this orbital, and there is four-electron deficiency. So even though the La atom offers three electrons, the HOMO still cannot be completely filled like in $Co_{13}$, which means that the $Fe_{13}$ cluster in
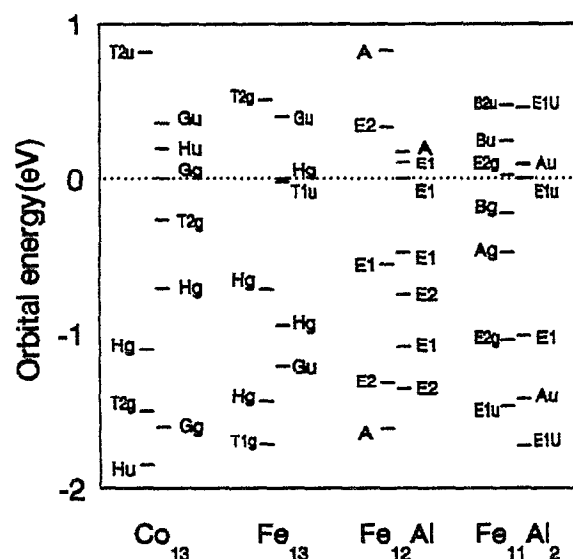


FIG. 1. The binding energy curves vs radial bond distance for $Co_{13}$, $Fe_{12}Al$, and $Fe_{11}Al_2$ clusters.



FIG. 2. Energy spectra of the isolated $Co_{13}$, $Fe_{12}Al$, and $Fe_{11}Al_2$ clusters.

LaFe$_{13}$ alloy cannot be stable. All these results are consistent with experimental facts.[1,2] To see the influence of substituting Fe by Al on the stability and properties of La(Fe$_x$Al$_{1-x}$)$_{13}$ alloys, we have studied the Fe$_{12}$Al and Fe$_{11}$Al$_2$ clusters, which represent the alloys at the different region of a magnetic phase diagram. The experiments have already found that the Al atom did not occupy the center of the icosahedron,[3] so we chose Fe$_{12}$Al, with $D_5$ symmetry. From the eigenspectrum in Fig. 2, we can see the HOMO is two-fold degenerate, with only one electron in it, the two-fold degenerate lowest unoccupied molecular orbital (LUMO) is also very close to the HOMO, three electrons provided by the La atom can fill the one electron deficiency in HOMO and also fill the two-fold degenerate LUMO; consequently, the Fe$_{12}$Al has a closed electron shell and becomes stable, which might be the reason why the experiment found the Fe$_{12}$Al alloys stable. In a similar way, we can expect that the Fe$_{11}$Al$_2$ would be stable in the La(Fe$_x$Al$_{1-x}$)$_{13}$ alloys.

In Table I, we have presented the magnetic moment for all calculated clusters, we have obtained the Co atom with 2.38$\mu_B$ magnetic moments, which is in good agreement with other theoretical and experimental results.[10,11] We have also obtained a large average magnetic moment (3.38$\mu_B$) for the free icosahedral Fe$_{13}$ clusters, and observed the magnetic moments for the atom at the center of the icosahedron are parallel to the magnetic moments for the atoms at the vertexes, which suggest that the ground state of the Fe$_{13}$ cluster be ferromagnetic, in agreement with other theoretical calculations.[12] When doping with Al, we find the cluster expands and the magnetic moments decrease. This occurrence of decrease of the magnetic moments can be attributed to that more and more iron atoms will lose their magnetic moments when Fe concentration decreases. This is confirmed by our studies on the Fe$_{11}$Al$_2$ clusters with D$_{5d}$ symmetry; we have found the magnetic moments for Fe atoms in Fe$_{11}$Al$_2$ are even smaller than that in Fe$_{12}$Al cluster. Hence, based on the results of the present cluster model calculations, it can be expected to get Pauli paramagnetism when decreasing the iron concentration and consequently decreasing the magnetic interaction, which is in agreement with the complicated experimental magnetic phase diagram of La(Fe$_x$Al$_{1-x}$)$_{13}$ alloys. In all the embedded clusters, we find a very similar eigenvalue spectra to the isolated clusters discussed above, so the same idea can be applied to stability of the embedded clusters, which have included the influence of the crystal field generated by 824 atoms. But we observed a small increase of magnetic moments with respect to the isolated clusters.

In summary, the electronic and magnetic properties of the four NaZn$_{13}$-type compounds, LaCo$_{13}$, LaFe$_{13}$, LaFe$_{12}$Al, and LaFe$_{11}$Al$_2$ have been studied by modeling those alloys by cluster on the basis of density functional theory. We found the relative stability as well as electronic structure of NaZn$_{13}$-type alloys can be explained according to its local icosahedral structural units. The main role of Al is to modify local electronic structure; this may facilitate the formation of the stable NaZn$_{13}$-type structure for the La–Fe alloys. In addition, the change of local magnetic properties with the change of Al concentrations bears resemblance to that of the alloys.

[1] T. T. M. Palstra, G. J. Nieuwenhuys, J. A. Mydosh, and K. H. J. Buschow, Phys. Rev. B **31**, 4623 (1985).

[2] R. B. Helholdt, T. T. M. Palstra, G. J. Nieuwenhuys, J. A. Mydosh, A. M. Van der Kraan, and R. H. J. Buschow, Phys. Rev. B **34**, 169 (1986).

[3] E. Matsubara, Y. Waseda, T. H. Chiang, and K. Fukamichi, Mat. Trans. JIM, **33**, 155 (1992).

[4] A. M. Van der Kraan, K. H. J. Buschow, and T. T. M. Palstra, Hyperfine Interact. **15/16**, 717 (1983).

[5] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).

[6] D. E. Ellis and G. S. Painter, Phys. Rev. B **2**, 2887 (1970).

[7] R. S. Mulliken, J. Chem. Phys. **23**, 1841 (1955).

[8] B. I. Dunlap, Phys. Rev. A **41**, 5691 (1990).

[9] X. G. Gong and V. Kumar (unpublished).

[10] Z. Q. Li and B. L. Gu, Phys. Rev. B **47**, 13 611 (1993).

[11] D. M. Cox, D. J. Trevor, R. L. Whetten, E. A. Rohlfing, and A. Kaldor, Phys. Rev. B **32**, 7290 (1993).

[12] O. B. Christensen and M. L. Cohen, Phys. Rev. B **47**, 13 643 (1993).