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Evidence for a new class of solids. First-principles study of $K(Al_{13})$

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Abstract

The stability of the crystalline phase of a cluster-assembled solid $K(Al_{13})$ has been investigated using first-principles total energy calculations. We find that $K(Al_{13})$ may form in the CsCl structure with a lattice constant of 6.52 Å. Unlike the gas phase, in which the ground state of the Al_{13} cluster is icosahedral, the Al_{13} becomes cuboctahedral in the solid phase due to crystal field effects. The system is metallic and is stable against lattice distortions. The calculations suggest that a new metastable solid could be made from two immiscible elements through specially designed synthesis processes.

In recent years, research on atomic clusters has added a new dimension to materials science, providing opportunities to make novel materials with unusual properties. It is now possible to not only make specific clusters in the gas phase but also to assemble them into solids not found in nature. The best-known example is the discovery of various crystalline phases that incorporate C_{60} [1]. In this Letter, we present powerful evidence for another type of cluster-assembled solid comprised of simple metals that are thought to be immiscible over their entire composition range.

Recently, Khanna and Jena [2] have suggested interesting possible structures involving clusters as building blocks. Reasoning from the similarity between the electronic structure and chemistry of atoms and metallic jellium clusters, they proposed that one can consider certain metal clusters as ‘giant atoms’ and that a new class of solids can be built with them.

The proposal is that the stability, geometry, and electronic properties of clusters may be manipulated by changing their size and composition, stable clusters can then be incorporated into solid phase materials as new meta-atoms. Consider, for example, an Al_{13} cluster. It has 39 valence electrons, one short of completing the outermost electronic shell [3,4]. The stability of this meta-atom will be enhanced substantially by adding one more electron to close the shell. It can then form ionic bonds with alkaline atoms just as a halogen atom does. Earlier cluster calculations for $K(Al_{13})$ molecules have shown this to be the case [4]. Based on this reasoning, a hypothetical solid phase of $K(Al_{13})$ was proposed.

In this Letter we provide evidence for a CsCl-structure $K(Al_{13})$ based on first-principles pseudopotential total energy calculations and give some quantitative details of its structural, dynamic and electronic properties. The characteristics of this phase are

somewhat different from Khanna and Jena's original predictions. It is expected that the new phase may require new cluster synthesis techniques.

We have carried out first-principles total-energy and force calculations within the local density approximation. The electronic solution is obtained via a preconditioned conjugate gradient algorithm [5]. The ultrasoft pseudopotential scheme of Vanderbilt was used [6]. For the K pseudopotential, two non-local projectors were used for the s and p wave functions, with a cutoff of 1.85 au. For Al, one non-local projector was used for the s and p wave functions, with a cutoff of 1.7 au. These pseudopotentials give bulk lattice constants for K and Al within a few percent of the experimental values. The details of generating the K and Al pseudopotentials will be published elsewhere [7]. In the solid state calculation, a plane wave cutoff of 20 Ry was used and the irreducible Brillouin zone was sampled with 24 special k -points in the simple cubic unit cell for T_h point group symmetry and 20 k -points for O_h symmetry (see discussion below). To account for the metallic nature of the system, the one-electron Kohn–Sham eigenvalues were broadened with a Gaussian distribution with a width of 0.1 eV to determine occupation numbers and the Fermi energy [8].

Because AB compounds of ions of dissimilar size tend to form in the CsCl structure¹, we first arranged the K atom and the Al_{13} cluster in this structure and constrained the Al_{13} cluster to obey T_h point group symmetry (T_h is a subgroup of both the icosahedral and octahedral groups). Four Al atoms are placed at corners of rectangles in x -, y -, and z -planes as shown in Fig. 1, and one Al at the center. The structure is uniquely defined by two characteristic lengths $L1$ and $L2$, the two edges of the rectangles. When $L1 = L2$ the structure becomes cuboctahedral. For $L1/L2 = 1.618$, the golden section value, the structure is icosahedral. The total energy and forces were minimized at a few selected volumes to obtain optimal energies and $L1/L2$ ratios. The $L1/L2$ ratio gradually decreases as the volume de-

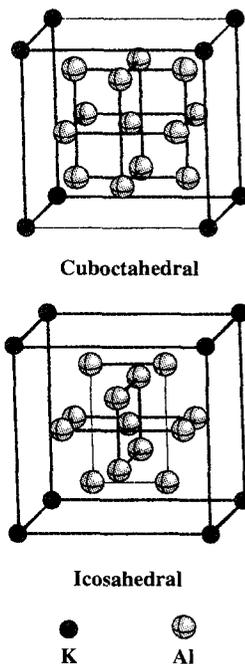


Fig. 1. Structures of $K(Al_{13})$ with icosahedral and cuboctahedral Al_{13} clusters. The x , y and z directions lie along the cube edges between K atoms.

creases, indicating that the structure will transform to octahedral symmetry at smaller volumes. The calculations were then repeated with the Al_{13} cluster subject to O_h point group symmetry.

In Fig. 2 we plot the binding energies as a function of volume for both structures. For the refer-

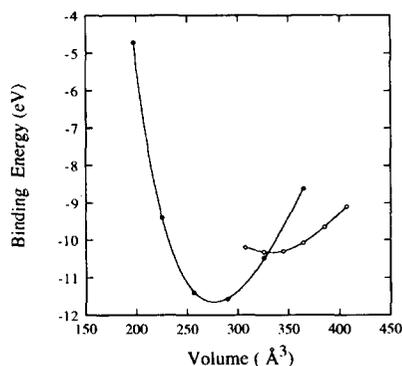


Fig. 2. Binding energies as a function of volume for $K(Al_{13})$ with T_h (open circles) and O_h (solid circles) Al_{13} clusters. The continuous curves are the results of the Murnaghan fits.

¹ We have also arranged the K atom and the Al_{13} cluster into a NaCl structure; the calculated energies are much higher than those in the CsCl structure.

ence energies of the K atom and the Al_{13} cluster, we used a simple cubic super cell with a lattice constant of 16 Å and the Γ point to sample the Brillouin zone. Our calculated Al_{13} cluster structure, with a distance of 2.62 Å from the central atom to a surface atom and a binding energy of 41.73 eV, is in excellent agreement with earlier calculations done with a similar technique [9]. At large volumes, we found that the structure with T_h symmetry is more stable than the one with O_h symmetry, and the $L1/L2$ ratios in the icosahedral-type structures are very close to the ideal value of 1.618. This is consistent with our cluster calculations [7] and other previous studies [4,9,10] which show the ground state of the Al_{13} cluster in the gas phase has icosahedral symmetry. At large volumes, the interactions between K– Al_{13} and Al_{13} – Al_{13} are weak, and the energetics within the cluster itself dominates its structure. At small volumes (below 340 Å³ or $a = 7$ Å), the stability of the two phases reverses and the cuboctahedral structure becomes more stable. This is due to stronger interactions between K– Al_{13} and Al_{13} – Al_{13} in this regime. Since the potassium atoms are arranged on a cubic lattice, their crystal field has O_h symmetry which eventually drives the Al_{13} cluster into O_h symmetry as well. This crystal field effect is also reflected in a decreasing $L1/L2$ ratio for the icosahedral structures as the volume decreases; $L1/L2$ drops from 1.71 to 1.44 as the volume changes from 407 to 307 Å³. At a volume of 289.4 Å³, the $L1/L2$ ratio actually becomes 1, so the icosahedral structure becomes cuboctahedral even with the T_h symmetry constraint. Also, at small volumes including the equilibrium volume, the shortest Al–Al distance is not within the Al_{13} cluster but between clusters which leads to strong interactions that make the system metallic. The cuboctahedral structure of the Al_{13} cluster is fcc-like within the cluster, with the central atom surrounded by twelve nearest neighbors. However, the environment of an Al atom on the outside of the cluster is not fcc-like, but quite different; each has five Al neighbors within the cluster and two in adjacent clusters. Furthermore, the volume per atom in our structure (including both K and Al) is about 20 percent larger than in fcc Al.

A Murnaghan equation of state was fitted to the calculated results to obtain the equilibrium volume V , the binding energy E_b , and the bulk modulus B

Table 1

Structural and elastic properties of $\text{K}(\text{Al}_{13})$. Elastic constants are in units of 10^{12} dyn/cm²

a	E_b	B	C_{11}	C_{12}	C_{44}
6.52 Å	–11.57 eV	0.54 Mbar	1.19	0.22	0.18

for the more stable cuboctahedral structure. The results are given in Table 1. The equilibrium volume is 277.17 Å³ which corresponds to a lattice constant $a = 6.52$ Å. The binding energy of 11.6 eV per $\text{K}(\text{Al}_{13})$ unit is substantially larger than that of molecular $\text{K}(\text{Al}_{13})$ (3.04 eV) [4]. This large binding energy makes it energetically favorable for this structure to be formed if potassium atoms and Al_{13} clusters could be brought together, although the structure is metastable since it has a positive formation energy in reference to bulk bcc K and fcc Al. However, it is well known that K and Al are immiscible [11], which presents a possible instability toward segregation for any structure of a K–Al compound. For this to occur, the structure would also be unstable to lattice distortions. To further test the structural stability, we have therefore calculated the elastic constants. Following Yin and Cohen [12], we first introduced a homogeneous tetragonal strain by scaling the three lattice parameters by $1 + \epsilon$, $1 + \epsilon$, and $(1 + \epsilon)^{-2}$, respectively, while keeping the volume constant. It can readily be shown that the elastic energy E_e associated with this strain for a cubic system is related to the shear modulus $C_{11} - C_{12}$ by

$$E_e = 3V(C_{11} - C_{12})\epsilon^2 + O(\epsilon^3). \quad (1)$$

The third order term is eliminated by averaging $E_e(\epsilon)$ and $E_e(-\epsilon)$. In the calculation, we varied the value of ϵ from 0 to ± 0.015 . Also, for a cubic system, the bulk modulus B which we have already obtained is related to C_{11} and C_{12} by

$$B = \frac{1}{3}(C_{11} + 2C_{12}). \quad (2)$$

To determine C_{44} , we introduced a strain in which one unit cell dimension was changed from $a\hat{i}$ to $a\hat{i} + \epsilon\hat{j}$, where a is the lattice constant. The values obtained for the elastic constants are given in Table 1. For comparison, measured values for pure Al are $C_{11} = 1.08$, $C_{12} = 0.62$, and $C_{44} = 0.28 \times 10^{12}$ dyn/cm². The fact that the elastic constants we obtained satisfy all three elastic stability criteria (C_{11}

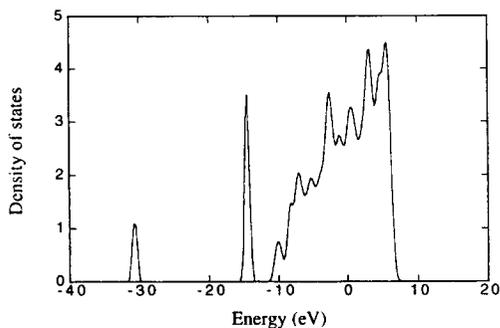


Fig. 3. Electron density of states of $K(Al_{13})$.

$+2C_{12} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$ [13] ensures structural stability against lattice distortions. This stability is very important since it implies the existence of an energy barrier to prevent segregation of the K and Al atoms into separate phases.

As another check on the sturdiness of the structure, we have done calculations of the lattice vibrations along major symmetry directions in the Brillouin zone using a simple ball and spring (Born–von Karman) model. Force constant parameters were estimated from the literature [14]. With reasonable estimates for the new structure, taking bond lengths into consideration, there are no negative eigenvalues (instabilities) or apparent soft modes.

The electron density of states at the equilibrium volume is plotted in Fig. 3. The Fermi energy E_F has been set as the zero point, and states up to 8 eV above E_F are included. As can be seen, there is the typical square root shape of a free electron density of states starting from -10 eV which is attributed to the Al 3s and 3p valence orbitals. In addition, there are two sharp peaks at about -30 and -15 eV which are due to the 3s and 3p shallow core states of potassium which are included in the calculations to improve the transferability of the potassium pseudopotential [7,15]. We find that the system is metallic rather than ionic as speculated at the outset based on stability arguments for the $K(Al_{13})$ cluster confined to a lattice with a large lattice constant [4]. As the potassium atoms and Al_{13} clusters are brought together to optimize their bonding, the Al_{13} clusters also come into closer proximity, and they interact strongly to make the whole system metallic. In fact, at the equilibrium lattice constant, the shortest Al–Al bonds are not within the Al_{13} clusters but rather

between neighboring clusters, with bond lengths about 7% smaller than in pure fcc Al. The Al–Al intra-cluster bond lengths are nearly the same as in pure Al. Nevertheless, ionic bonding between K and Al_{13} may still be very important to the formation of the structure, especially in early stages of synthesis.

It is possible that by changing the composition of the cluster or the alkali atom, the cluster-assembled solid could be made into an insulator or a semiconductor. The key is to increase the Al–Al distance between the clusters in the stable crystalline phase. This can perhaps be accomplished by replacing K by Cs. The larger size of the alkali ion would cause the lattice constant to increase. These studies are currently in progress.

To summarize, we have demonstrated that the cluster-assembled solid $K(Al_{13})$ may be formed based on first-principles total energy and lattice dynamics calculations. We predict a new metastable crystalline phase with the CsCl structure, lattice constant $a = 6.52 \text{ \AA}$, and bulk modulus $B = 0.54$ Mbar. The system is metallic. Our study presents a unique example that with modern technology, one might be able to make completely new solid state alloys from two immiscible elements by first confining one of them into clusters. While pure Al_{13} clusters are likely to coalesce to bulk fcc Al metal in the condensed phase [10], the structure we have discussed might perhaps be amenable to synthesis by first decorating each Al_{13} cluster with a K atom to form a stable $K(Al_{13})$ molecule and then bringing these together to form the solid. We await and encourage experimental efforts.

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References

- [1] W. Krättschmer, L.D. Lamb, K. Fostiropoulos and D.R. Huffman, *Nature* (London) 318 (1990) 354.
- [2] S.N. Khanna and P. Jena, *Phys. Rev. Letters* 69 (1992) 1664.

- [3] W.D. Knight, K. Clementer, W.A. de Heer, W.A. Saunders, M.Y. Chou and M.L. Cohen, *Phys. Rev. Letters* 52 (1984) 2141.
- [4] S.N. Khanna and P. Jena, *Chem. Phys. Letters* 219 (1994) 479.
- [5] M.P. Teter, M.C. Payne and D.C. Allan, *Phys. Rev. B* 40 (1989) 12.
- [6] D. Vanderbilt, *Phys. Rev. B* 41 (1990) 7892.
- [7] F. Liu et al., to be published.
- [8] C.-L. Fu and K.M. Ho, *Phys. Rev. B* 28 (1983) 5480.
- [9] A.P. Seitsonen, M.J. Puska, M. Alatalo and R.M. Nieminen, V. Milman and M.C. Payne, *Phys. Rev. B* 41 (1990) 7892.
- [10] H.P. Cheng, R.S. Berry and R.L. Whetten, *Phys. Rev. B* 43 (1991) 10647;
- J.Y. Yi, D.J. Oh, J. Bernholc and R. Car, *Chem. Phys. Letters* 174 (1990) 461;
- X.G. Gong and V. Kumar, *Phys. Rev. Letters* 70 (1993) 2078.
- [11] L.F. Mondolfo, ed., *Aluminum alloy: structure and properties* (Butterworth, London, 1976).
- [12] M.T. Yin and M.L. Cohen, *Phys. Rev. B* 26 (1982) 3259.
- [13] M. Born and K. Huang, *Dynamical theory of crystal lattices* (Clarendon Press, Oxford, 1956);
J. Wang, S. Yip, S.R. Phillpot and D. Wolf, *Phys. Rev. Letters* 71 (1993) 4182.
- [14] G. Gilat and R.M. Nicklow, *Phys. Rev.* 143 (1966) 487.
- [15] F. Liu, S.H. Garofalini, R.D. King-Smith and D. Vanderbilt, *Chem. Phys. Letters* 215 (1993) 401.