Caged clusters in Al$_{11}$Ir$_4$: structural transition and insulating phase

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Using pair potentials fitted to an ab-initio database, combined with replica-exchange simulated annealing, we show the complex, quasicrystal-related Al$_{11}$Ir$_4$ compound contains a new version of the “pseudo-Mackay” icosahedral cluster, with non-icosahedral inner Al$_4$Ir and/or Al$_6$Ir clusters that exist in various orientations and account for partial occupancies in the reported structure. Two different compositions show first-order transitions to orientationally ordered phases doubling the (cubic) unit cell, which are respectively metallic and insulating.

PACS numbers: 02.70.Ns, 61.50.Lt, 63.20.Dj, 64.70.Kb, 61.44.Br

Al$_{11}$Ir$_4$ is a phase in one of the complex metallic alloy systems that resist ordinary approaches to determining crystallographic structure or phase diagrams, because of two impediments to equilibration at low temperatures: (1) there are numerous competing complex phases of similar composition (2) the intermediate-temperature structures have inherent entropy associated with block rearrangements of tiles or clusters.

Despite the measurement of 457 independent reflections, the experimentally refined structure [1] of Al$_{11}$Ir$_4$ has twice as many sites listed as atoms, many with a fitted occupancy of less than 0.5. Until occupancy correlations are known, such structure knowledge is inadequate for computing electronic properties or total energies.

Instead, in this letter we predict the structure, aided by its close relationship to Al-transition metal (Al-TM) quasicrystals. These are described as networks of identically oriented icosahedral clusters linked along certain symmetry directions [2], e.g. the “Mackay icosahedron” [2] consisting of an empty center plus two concentric shells of full icosahedral symmetry, Al$_{12}$ + Al$_{30}$Mn$_{12}$.

It is generally accepted that the stable quasicrystals i-AlCuFe and i-AlPdMn contain a modified cluster called the “pseudo Mackay icosahedron” (pMI) in which the inner Al$_{12}$ icosahedron is replaced by a cluster with fewer atoms and reduced symmetry [3], the details of which are still unclear. We note that the Ca–Cd quasicrystals, another major class along the Al–TM quasicrystals, and complex alloys related to them, also contain icosahedral clusters with an inner shell of lower symmetry [4] – a tetrahedron, in that case. Thus, such inner rotatable clusters may be a common feature of well-ordered quasicrystal systems, and they presenttractable examples of the above-mentioned block-rearrangement degrees of freedom.

In the rest of this paper, we uncover the correct low-$T$ structure of Al$_{11}$Ir$_4$ using energy minimization, in several stages. We used both ab-initio codes (VASP package [5]) and empirically fitted pair potentials. First we determined the possible atom contents of one cluster to be Al$_5$Ir or Al$_{10}$Ir. Next, for each cluster, we find its atom arrangement and preferred orientation within the cage of neighboring atoms. The partially occupied sites in the refined structure [1] are explained with an equal mixture of the two kinds of cluster. We also find the collective ordering of orientations and identify the ordering transition. The equal-mixture phase is metallic, as seen in experiment [25], but the composition with Al$_{10}$Ir clusters is predicted to be insulating.

As a prerequisite to exploring alternative structures and running extensive molecular dynamics (MD) simulations, we generated “empirical oscillating pair potentials” (EOPP) valid for Al–Ir in this composition range, using the method of Ref. [6] to fit a database of ab-initio forces, calculated with VASP [5]. The database contained snapshots from ab-initio molecular dynamics simulations at high temperatures, as well as $T = 0$ structures of various stable and unstable Al–Ir structures, in particular the Al$_{12}$Pd$_8$ and B2 structures. (The functional form and fitted coefficients of the potentials are provided in the supplementary material [10].)

**Structural optimization of individual cluster in Al$_{11}$Ir$_4$** — The reported crystal structure of Al$_{11}$Ir$_4$ is a simple cubic arrangement of pMI clusters, each having an inner shell of ~ 40 partially occupied sites with combined occupancy 10. Surrounding this is the second shell, an Ir$_{12}$ icosahedron, plus 30 Al sites slightly outside that icosahedron’s mid-edges, of which the six sites along cubic 2-fold axes are only partially occupied. Between the pMI clusters, at each body center, is an Ir atom, surrounded by an icosahedron of 12 Al atoms, which are shared with the pMI in the role of second-shell Al. The key fact to determine by energy optimization is the atom configuration in the uncertain, inner-shell sites.

The first question about the inner Al cluster is how many atoms it (optimally) contains. We addressed this directly by constructing initial configurations of the Al$_{11}$Ir$_4$ unit cell with a chosen number $m$ of inner Al atoms (assuming the periodicity of only one unit cell). The configuration was optimized, first by annealing with molecular dynamics (MD) using the fitted EOPP potentials at fixed volume; this was followed by ab-initio relaxation using VASP [5], optimizing all structural parameters. [9]. The first stage was annealing in one unit cell...
In its optimum orientation (of multiplicity 12), the 10-cluster is tilted rigidly so as to bring its threefold axis closer to (but not quite parallel to) the nearby (100) axis, as seen in Figure 1(b). That brings the apical capping Al and all three of the side-capping Al atoms (which are farther out from the central Ir) close to cubic (100) axes, and they merge with the Al atoms of the pMI’s second shell (cage) that sit in the same direction. The pMI clusters in Fig. 1 overlap along the [100] direction such that some outer shell atoms of one pMI also belong to the inner cluster of the neighboring pMI [12].

At $T \approx 600 K$, just 100K above the orientational $T_c$ (see below), an inner Al$_{10}$Ir cluster spends 95% of the time close to one of the twelve ideal orientations described above (as shown by quenching a crystal using Al$_{10}$ filling in each cage.) At higher temperatures, the threefold axis of the 10-cluster may instead align along a cubic (111) axis, or a pseudo 2-fold axis (of the Ir$_{12}$ cage). (We have not examined the high-$T$ orientations of the 9-cluster.)

The Al partial occupancies refined in [1] are in close agreement with our model, provided that close to half the clusters are 9-clusters and half are 10-clusters, and each is oriented independently in one of the (respectively) six or 12 optimum orientations. [11] (Fig. 2(a)) shows the time-averaged atom density from a high-$T$ simulation, containing lines of closely spaced alternative sites. The refined Al(3) and Al(4) sites of [11] represent this spread-out density, coming from four or five model sites of both 9- and 10-clusters; the reported Al(2) and Al(5) sites comes respectively from one site of the 9-cluster and two sites of the 10-cluster in our model, showing that both clusters must be present. The r.m.s. discrepancy between predicted and reported occupancies of each site is ~12% of the occupancy [10].

Orientational ordering — To address the statistical mechanics of systems with many interacting clusters, we set up a replica-exchange [7] simulation in a $4 \times 4 \times 4$ supercell, i.e. 1920 atoms (10-phase), annealing 16 independent samples, each at a different temperature, spanning 310K to 460K; additional single-$T$ simulations were done at higher temperatures.

The simulated alloy remains solid beyond 1700 K in 2x2x2 supercell (the experimental melting point is above 1600 C for $x_{Ir} \sim 0.27$ [13]). The simulation lasted 4000 cycles, each consisting of 1000 molecular dynamics (MD) steps with time increment $\Delta t=5$ fs, for a total simulation time 20 ns. The pair-potential interaction radius was cut off at $r_c=10 \AA$. [8]. The initial state for the MD was our best single-cell model, repeated in all 4$^3$ cells.

The low-temperature optimal structures of the 9.5-phase and 10-phase were determined by rapidly quenching configurations from the lowest replica ($T = 310K$) to a $T = 0$ energy minimum, and selecting those with the lowest relaxed energies. In 9.5-phase, the structure was a stack along (say) the $z$ direction of layers which

![FIG. 1: Inner clusters in Al$_{11}$Ir$_4$ structures, shown as they order in the low-$T$ “9.5 phase”. The surrounding icosaedron of black atoms is the Ir$_{12}$ “cage”; another Ir atom is at center. The “apex” Al atoms are shown gray. (a). Al$_4$Ir clusters in $z = 0$ plane of the “9.5 phase” with their 4-fold axes oriented up and down along viewing $z$ axis, (b). Al$_{10}$Ir clusters in $z = 0.5$ plane, with their 3-fold axis almost parallel to the viewing $z$ axis . (c). Orientation relation of two Al$_4$Ir clusters (left) with two Al$_{10}$Ir clusters (right), viewd along $x$ direction. The layers of identical-content clusters are stacked normal to the page in (a) and (b), or left to right in (c), in a checkerboard pattern. In the 10 phase, 10-cluster arrangement in (b) is repeated in $2 \times 1 \times 1$ supercell.

Table I: Relaxed energies (in meV/atom) as a function of Al per pMI inner cluster. Supercell used was $2 \times 2 \times 2$, except $4 \times 4 \times 4$ for the 10 Al case. Last row is mean lattice parameter, per fundamental cell.

| inner cluster | Al | 8 | 9 | 9.5 | 10 | 11 | 12 |
|---------------|----|---|---|-----|----|----|----|
| supercell     | +45 | +33 | - | +10 | +77 | +132 |
| $a_{cub}$ [Å] | 7.64 | 7.68 | 7.70 | 7.73 | 7.78 | 7.82 |

(see Table I), to identify energy differences: this excluded the $m = 8$, $m = 11$ and $m = 12$ variants, leaving only the $m = 9$ and $m = 10$ ones which we “9-cluster” and “10-cluster” from here on. In a second stage, we annealed in a supercell to accomodate possible alternations of the orientations, and found two nearly stable structures: the $m = 10$ filling (“10-phase”) and an equal mixture of $m = 9$ and $m = 10$ fillings (“9.5-phase”). From here on, in studies of the whole structure, we limit ourselves to these two fillings.

The 9-cluster is almost always a square antiprism, with one square enlarged and capped by an additional Al atom [see Fig 1(a)]. In its optimum orientation (of multiplicity six), the fourfold axis is aligned with one of the cubic (100) axes, with the outer square of atoms in mirror planes. The 10-cluster is practically always a sort of trigonal prism, with one triangular end face enlarged and capped by an atom, and also capped on the three trapezoidal side faces.
had a $\sqrt{2} \times \sqrt{2}$ checkerboard pattern of inner clusters, with their main (fourfold or threefold) axes alternating between $+z$ and $-z$ directions; the layers are stacked such that the overlaying clusters have the same orientation of main axes. (To fully specify their orientations, note the 10-clusters of $+z$ and $-z$ alignment are always related by a mirror reflection in the $xy$ plane.) The relation between adjoining clusters is shown in Figure [1].

In the 10-phase, the 10-clusters pair shown in Fig. [1]b) is repeated in the supercell doubled along $y$ direction. The crystal structures are summarized in Table [II] coordinates are available in Ref. [10].

The ordered arrangement of the 9.5 phase contains alternating (square) layers of 9-clusters and 10-clusters. Each layer is made by repeating Fig. [1]a) or (b) in both directions: thus, within either kind of layer, the apex directions alternate up and down. These layers are stacked without shifts so that chains of identically aligned clusters run perpendicular to the plane of the layers.

We pinpointed the ordering temperature of the “10” phase in three ways. Firstly, we can examine the atom density distribution, averaged over moderate times (Fig. [2]a); for $T > T_c$ this has the full symmetry of the unit cell, but for $T < T_c$ this shows (despite some fluctuations) a clear symmetry breaking (to the cell-doubled structure just described). A second evidence for a phase transition is available within the replica-exchange simulation: a larger energy spacing $\Delta E_i = E(T_i) - E(T_{i-1})$ between the replicas at consecutive temperatures, suggesting a latent heat. The third and most convincing signature is that, for a finite system, the ensemble at temperatures close to $T_c$ is a mixture of the two phases, weighted according to the difference in their free energies. This is evident in Fig. [2]b), from which we can read off $T_c \approx 495K$. The peak separation in Fig. [2]b) shows that the ordered and disordered states in the 10-phase differ by (a latent heat of) 3 meV per atom, requiring an entropy difference at $T_c$ of (30)(3 meV)/$T_c \approx 10(9)$ per 30-atom cell. That is, we have effectively $N_{cs} \approx 9$ states per cluster, comparable with $N_{cs} = 12$ ideal orientations.

The 9.5 phase has two kinds of order – the 9Al/10Al alignment in cluster content and the orientations – which might appear in separate transitions. The first ordering requires vastly longer equilibration times (for intercluster Al diffusion) and we were unable to identify any sharp transitions.

Phase stability in Al–Ir system — We now turn to the $T = 0$ phase stability of Al$_{11}$Ir$_4$ and other Al–Ir compounds. The currently accepted Al–Ir phase diagram [15] with $0 < x_{Ir} \leq 0.5$ shows six compounds as stable: Al$_9$Ir$_2$ (in the Al$_9$Co$_2$ mP22 structure); AlIr; and around $x_{Ir} \approx 1/4$, there is Al$_5$Ir$_3$ plus the complex phases Al$_{11}$Ir$_4$, Al$_{28}$Ir$_9$ [14] and orthorhombic Al$_{25}$Ir$_{13}$ [15]. We additionally tried other complex phases structures not reported in Al–Ir, among them: (i) Al$_{15}$Ir$_8$ in the Al$_{21}$Pd$_8$ structure, [16] which is a packing of sixteen of our 10-clusters per unit cell, without any icosahedral cages (and sharing a few Al atoms). (ii) Al$_{14}$Ir$_{23}$ in the Al$_{31}$Cu$_8$Ir$_{15}$ structure [14], equivalent to Al$_{60}$Pd$_{20}$Ru$_{12}$ [19] and Al-CuRuSi [20]; here the even-vertex clusters alternate between an Al$_{10}$Ir trigonal cluster and an AlCu$_8$Al$_6$ cluster, identical to atomic arrangement in B2 cubic structure.

Of these, the available structures of Al$_{11}$Ir$_4$ and Al$_{28}$Ir$_9$ include many fractional sites, so in total energy calculations we had to try versions of these structures with various ways of realizing the occupations. The relaxed total energies of all these compounds (and the pure elements) were computed using VASP. [19] We found AlIr and Al$_9$Ir$_2$ to be stable, as expected; the only stable phases around $x_{Ir} \approx 1/4$ were Al$_{15}$Ir$_3$ and (surprisingly) Al$_{21}$Ir$_8$. Relative to a corrected tie-line including Al$_{21}$Ir$_8$, we found Al$_3$Ir to be unstable by 25 meV/atom; this is reduced to only $\sim 8$ meV/atom in a variant (Al$_{17}$Ir$_6$) with a tripled cell in which one Al is removed. Thus, in contradiction to Ref. [13] we believe Al$_3$Ir is a high-temperature
phase only. The phases Al$_{11}$Ir$_4$, Al$_{28}$Ir$_9$, and Al$_{11}$Ir$_{14}$ in the 9.5-phase were unstable by rather small amounts of 6, 7, and 9 meV/atom, respectively; in the latter two, the site disorder contributes entropy which may explain their stability at higher temperatures. The heat of formation for Al$_{11}$Ir$_4$ is large: $-0.738$ eV/atom; for Al$_{21}$Ir$_8$ it is $-0.760$ eV/atom (see Supplementary material for detailed information on formation energies and stability data for all discussed phases).

**Electronic density of states** — A specific interest in Al–Ir and certain other Al–TM systems is the possibility of an insulating alloy, the elemental constituents of which are all good metals, e.g. Al$_2$Ru in the TiS$_2$ structure [24], Al$_2$Fe in the MoS$_2$ type-structure [21, 22]. Quasicrystal i-AlPdRe (built from pMI clusters) is long claimed to be a semiconductor [23, 24]. Predicting gap formation in these alloys depends critically on the accurate relaxation of atomic positions [23].

We find the Al$_{11}$Ir$_4$ electronic density of states (DOS) in the ordered ($T = 0$) “10” phase has a narrow gap, and significant pseudogap as shown in Fig. 3, so this alloy should be a semiconductor. By contrast, the ordered “9.5” phase is predicted to be robustly metallic [Fig. 3(b)] (In the disordered high-temperature “10” phase [not shown] the gap tends to get filled in, so that phase is also likely to be metallic.) We call attention to the fact that these very similar structures have radically different electronic properties, all due to details of the placement of certain Al atoms that link adjacent clusters.

**Discussion** — In conclusion, starting from diffraction data refined average structure of Al$_{11}$Ir$_4$ [1], we combined molecular dynamics simulations with pair potentials to discover a well-defined, asymmetric inner Al$_9$Ir and Al$_{10}$Ir clusters, with variable orientations, and an ordering transition to new orthorhombic phases. We suggest an experimental search for the ordered phase having all clusters of Al$_{10}$Ir type, as it has a gap exactly at the Fermi energy, and hence should be a semiconductor. We also found that, contrary to the accepted phase diagram, the stable low-temperature phase at $x_{Ir} \approx 1/4$ is Al$_{12}$Ir$_8$.

Several other known structures are made by placing pMI clusters and/or variants on the same simple cubic lattice with $a \approx 7.7$Å: not only Al$_{41}$Cu$_8$Ir$_{15}$, [18], Al$_{58}$Pd$_{25}$Ru$_{12}$ [19] and AlCuRuSi [20], which we mentioned, but also Al$_{70}$Pd$_{10}$Fe$_{20}$ [29], and $\epsilon$-Ag$_{75}$Mg$_{25}$ (in the latter case, the “even”-node inner clusters are AgMg$_8$ cube, while “odd” nodes are perfect Mackay icosahedra).

Furthermore, the lowest energy version yet found of the i-AlPdMn quasicrystal structure [26, 27] consists of exactly the same pMI clusters described above, in particular (i) they have a short ($\sim 8$Å) linkage along the icosahedral twofold direction, rather than the $\sim 12.5$Å linkage known from $\alpha$-AlMnSi [2] (ii) they have an Al$_{10}$Mn inner cluster in the same shape as the one described here, which appear in various orientations with only small energy differences. The decagonal-related $\xi'(AlPdMn)$ phase contains pMI clusters with Al$_6$Mn and Al$_{10}$Mn inner clusters, not quite identical to those we presented here.

The icosahedral cage containing an inner cluster that breaks icosahedral symmetry is known in a quite different family of quasicrystals and related compounds: CaCd$_6$ or ScZn$_6$, with an inner Cd$_4$ or Zn$_4$ tetrahedron [3, 30]. Those, too, show orientational orderings at low temperatures [31, 32]. We observe that, if there is any way at all in icosahedral quasicrystals to implement the long-sought “local matching rules” that would stabilize an ideal quasiperiodic ground state, or merely rules that limit tiling randomness to large spatial scales the likeliest candidate are these inner clusters that spoil the clusters’ high symmetry.

On the theoretical side, this work on Al–Ir could be extended in the following directions: (1) simulation of the inner-cluster dynamics for comparison to neutron data, analogous to the Cd$_4$ tetrahedron in CaCd$_6$ [30]; (2) fitting an orientational interaction between adjacent clusters [33] for Monte Carlo estimation of the orientational $T_c$. (3) a possible Al–Ir quasicrystal based on these clusters. Experimental clarification of the low–temperature stabilities of Al–Ir around $x_{Ir} \sim 0.27$ are of course highly desirable.

We thank W. Steurer and P. Kuczera for sharing structural data on Al$_{41}$Cu$_8$Ir$_{15}$ phase prior to publication, R. Tamura for fruitful discussions, and Yu. Grin for careful reading of the manuscript and comments, in particular pointing out cluster relationship with Al$_9$Mn structure. This work was supported by DOE Grant DE-FG02-
89ER-45405 (MM, CLH), and Slovak funding VEGA 2/0111/11 and APVV-0492-11 (MM).

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SUPPLEMENTARY INFORMATION

In this section, we give tables of three kinds of detailed information omitted from the main text of the paper.

Al–Ir phases for stability calculations

Table III gives the data used to find the predicted binary phase diagram of the Al–Ir system, by the usual convex-hull construction. Despite the structure names, a binary Al–Ir composition is used in all cases, with Ir replacing any transition metals. All energies are ab-initio calculations with the VASP code.

| structure | ΔE (meV/atom) | ΔH (meV/atom) | x(Al) % | x(Ir) % |
|----------|---------------|---------------|--------|--------|
| Al₂Co₂.mP22 | 0 | -544.0 | 81.8 | 18.2 |
| Al₁₅Ir₁₃.oP236 | -658.8 | 77.6 | 22.4 |
| Al₂₁Pd₈.t1116 | -759.6 | 72.4 | 27.6 |
| Allr.cP2 | -955.3 | 50.0 | 50.0 |
| Al₂Co₂.hP28 | 2.8 | -765.4 | 71.4 | 28.6 |
| Al₁₁Ir₄.oP60⁺ | 3.7 | -737.9 | 73.3 | 26.7 |
| Al₁₁Ir₂₃.hR64 | 5.6 | -826.9 | 64.1 | 35.9 |
| Al₂₈Ir₉.hP236 | 7.2 | -672.3 | 76.5 | 23.5 |
| Al₃Ir.hP24⁺ | 7.8 | -722.5 | 73.9 | 26.1 |
| Al₁₁Ir₂₃.oA236⁺ | 9.2 | -741.2 | 72.9 | 27.1 |

TABLE III: Energy diagram of Al–Ir system at T=0K. Column ΔE is energy in meV/atom by which a structure is unstable relative to a mixture of competing stable compounds. Stable compounds forming convex hull of energy–composition scatter plot have ΔE = 0.

a “10-phase”

b triple supercell of Al₃Ir, with one less Al atom (site vacant).

*c “9.5-phase”
Fitted pair potentials

Most calculations in the paper were based on empirical oscillating pair potentials (EOPP) of form

\[ V(r) = \frac{C_1}{r^{\eta_1}} + \frac{C_2}{r^{\eta_2}} \cos(k_r + \phi_*) \]  

as presented by Mihalković and Henley (main text Ref. [6]), where \( r \) is the distance between a pair of atoms. The fitted coefficients we used are listed in Table IV. Fig. 4 gives a scatter plot demonstrating the goodness of fit and a plot of the potentials themselves. As is typical of Al-transition metal (Al-TM) potentials, with TM=Ir in this case: (a) the Al-Al potential has no nearest-neighbor well but only a shoulder (b) the Al-Ir potential has a very deep well at the nearest-neighbor distance (c) the Ir-Ir potential is unfavorable for nearest neighbors but has a deep well at the second neighbor distance (d) all the potentials have relatively strong Friedel oscillations.

Crystal structure of phase with Al\textsubscript{10}Ir clusters

Table V lists all the Wyckoff positions of the low-temperature structure of the “10-phase” of Al\textsubscript{11}Ir\textsubscript{4}; The cluster orientations correspond to Figure 1(b) of the main text, corresponding to a cubic cell doubled in one direction (becoming the \( a \) direction); since the cubic structure lacks 4-fold symmetry, this causes the \( b \) and \( c \) cell parameters to become different by \( \sim 0.6\% \).

**TABLE IV:** Fitted parameters for Al–Ir EOPP potentials.

|                  | \( C_1 \)          | \( \eta_1 \) | \( C_2 \)          | \( \eta_2 \) | \( k_* \) | \( \Phi_* \) |
|------------------|-------------------|-------------|-------------------|-------------|-----------|------------|
| Al–Al            | \( 9.9811 \times 10^2 \) | 8.7044      | \( -11.3044 \times 10^2 \) | 5.4518      | 3.5646    | 2.5119     |
| Al–Ir            | \( 1.3764 \times 10^4 \) | 13.3271     | \( 9.2649 \times 10^2 \) | 3.8320      | 3.1919    | 1.1091     |
| Ir–Ir            | \( 3.2083 \times 10^5 \) | 12.7731     | \( -7.2818 \times 10^2 \) | 3.0765      | -2.8274   | 0.4493     |

**TABLE V:** List of Wyckoff sites for “10-phase” structure.

| site       | \( X \) | \( Y \) | \( Z \) |
|------------|--------|--------|--------|
| Ir1/2b     | 0.5000 | 0.5000 | 0.5135 |
| Ir3/2c     | 0.2500 | 0.4745 | 0.2897 |
| Ir5/4d     | 0.5028 | 0.7269 | 0.4935 |
| A11/4d     | 0.3668 | 0.8794 | 0.6644 |
| A11/3c     | 0.2500 | 0.6492 | 0.0013 |
| A1/8d      | 0.7498 | 0.0006 | 0.0008 |
| A1/4c      | 0.7499 | 0.2500 | 0.6054 |
| A1/5d      | 0.5001 | 0.8857 | 0.4935 |
| A1/7c      | 0.3602 | 0.0013 | 0.7517 |
| A1/9c      | 0.2506 | 0.7500 | 0.4015 |
| A1/11d     | 0.0006 | 0.3900 | 0.4985 |
| A1/12d     | 0.1609 | 0.3489 | 0.5097 |
| A1/14d     | 0.2355 | 0.9163 | 0.1491 |
| A1/16d     | 0.2433 | 0.8876 | 0.8458 |
| A1/18d     | 0.3340 | 0.3545 | 0.5409 |
| A1/20d     | 0.4067 | 0.9012 | 0.3482 |
| A1/22d     | 0.4571 | 0.7500 | 0.5829 |
| A1/24d     | 0.4199 | 0.2500 | 0.3960 |
| A1/26d     | 0.4944 | 0.9075 | 0.8078 |
| A1/28d     | 0.9035 | 0.9986 | 0.9101 |
| A1/30d     | 0.3622 | 0.8352 | 0.2877 |
| A1/32d     | 0.0351 | 0.0876 | 0.0008 |
| A1/34d     | 0.9061 | 0.9990 | 0.0003 |
| A1/36d     | 0.8504 | 0.7500 | 0.2500 |

**TABLE VI:** Atomic structure of “9.5-phase” (oA236) in space group Abm2 (\#39). Optimized lattice parameters are \( a=15.321 \text{Å}, b=15.475 \text{Å}, c=15.412 \text{Å} \). Cluster centers are Ir2 (“9-clusters”) and Ir7 (“10-clusters”).

| site       | \( X \) | \( Y \) | \( Z \) |
|------------|--------|--------|--------|
| Ir1/8d     | 0.7498 | 0.0006 | 0.0008 |
| Ir3/4c     | 0.7499 | 0.2500 | 0.6054 |
| Ir5/8d     | 0.5001 | 0.8857 | 0.4935 |
| Ir7/4c     | 0.5018 | 0.7500 | 0.2503 |
| Ir9/4c     | 0.2461 | 0.7500 | 0.3962 |
| Ir11/8d    | 0.0006 | 0.3900 | 0.4985 |
| Ir13/8d    | 0.1609 | 0.3489 | 0.5097 |
| Ir15/8d    | 0.2355 | 0.9163 | 0.1491 |
| Ir17/8d    | 0.2433 | 0.8876 | 0.8458 |
| Ir19/8d    | 0.3340 | 0.3545 | 0.5409 |
| Ir21/8d    | 0.4067 | 0.9012 | 0.3482 |
| Ir23/8d    | 0.4571 | 0.7500 | 0.5829 |
| Ir25/8d    | 0.4199 | 0.2500 | 0.3960 |
| Ir27/8d    | 0.4944 | 0.9075 | 0.8078 |
| Ir29/8d    | 0.9035 | 0.9986 | 0.9101 |
| Ir31/8d    | 0.3622 | 0.8352 | 0.2877 |
| Ir33/8d    | 0.0351 | 0.0876 | 0.0008 |
| Ir35/8d    | 0.9061 | 0.9990 | 0.0003 |
| Ir37/8d    | 0.8504 | 0.7500 | 0.2500 |
| Ir39/8d    | 0.4944 | 0.9075 | 0.8078 |
| Ir41/8d    | 0.9035 | 0.9986 | 0.9101 |
| Ir43/8d    | 0.3622 | 0.8352 | 0.2877 |
| Ir45/8d    | 0.0351 | 0.0876 | 0.0008 |
| Ir47/8d    | 0.9061 | 0.9990 | 0.0003 |
| Ir49/8d    | 0.8504 | 0.7500 | 0.2500 |

### FIG. 4: EOPP potentials fitted to ab-initio (VASP) force and energy datapoints. Fit to forces (left panel) is shown with fitted forces (vertical axis) plotted against VASP forces (horizontal axis). The fitted pair potentials are shown in the right panel. Parameters
TABLE VII: “9-phase” structure (aI232), space group *Ibam* (No. 72), orthorhombic lattice parameters are *a*=15.136 Å, *b*=15.517 Å, *c*=15.457 Å. “9-cluster” centers are at Ir2 site.

| site  | X    | Y    | Z    |
|-------|------|------|------|
| Ir1/4b| 0.5000 | 0.0000 | 0.2500 |
| Ir3/8j| 0.9954 | 0.3955 | 0.5000 |
| Ir5/16k| 0.2503 | 0.5011 | 0.3603 |
| Ir7/4a| 0.0000 | 0.0000 | 0.7500 |
| Al2/16k| 0.0877 | 0.9954 | 0.3987 |
| Al4/16k| 0.9124 | 0.5012 | 0.1026 |
| Al6/16k| 0.1544 | 0.0893 | 0.7501 |
| Al8/16k| 0.1403 | 0.3379 | 0.4147 |
| Al10/8j| 0.2925 | 0.4107 | 0.5000 |
| Al12/8j| 0.4193 | 0.2521 | 0.5000 |

TABLE VIII: Structure of rhombohedral Al_{41}Ir_{23} (hR64) phase, space group *R3* (No. 146) in hexagonal setting. Optimized lattice parameters are *a*=11.032 Å and *c*=27.073 Å. “10-clusters” surround Ir1 sites, Al1 site is center of “B2”-structure local environments.

| site  | X    | Y    | Z    |
|-------|------|------|------|
| Ir1/3a| 0.0000 | 0.0000 | 0.0020 |
| Ir3/3a| 0.0000 | 0.0000 | 0.2496 |
| Ir5/9b| 0.6312 | 0.0770 | 0.4618 |
| Ir7/9b| 0.3639 | 0.9178 | 0.5390 |
| Ir9/9b| 0.7434 | 0.8712 | 0.4665 |
| Ir11/9b| 0.2580 | 0.1292 | 0.5313 |
| Al2/9b| 0.8717 | 0.1251 | 0.4363 |
| Al4/9b| 0.2697 | 0.2245 | 0.2304 |
| Al6/9b| 0.0192 | 0.1585 | 0.1729 |
| Al8/9b| 0.7519 | 0.7866 | 0.7116 |
| Al10/9b| 0.9820 | 0.8361 | 0.8292 |
| Al12/9b| 0.5229 | 0.1744 | 0.4054 |
| Al14/9b| 0.8615 | 0.5862 | 0.3442 |

"10-clusters" surround Ir1 sites, Al1 site is center of “B2”-structure local environments.