

## Simulated structure and thermodynamic stability of the AlCoCu decagonal quasicrystal

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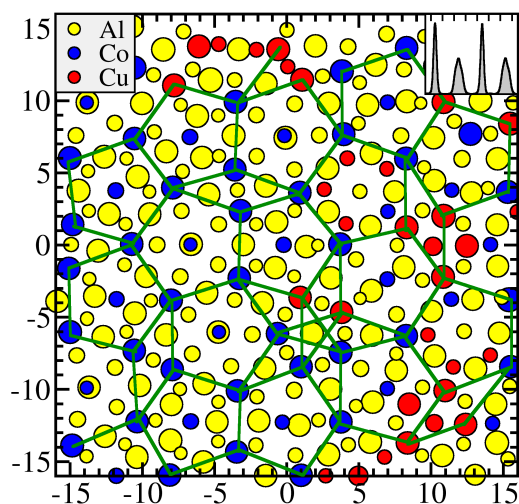
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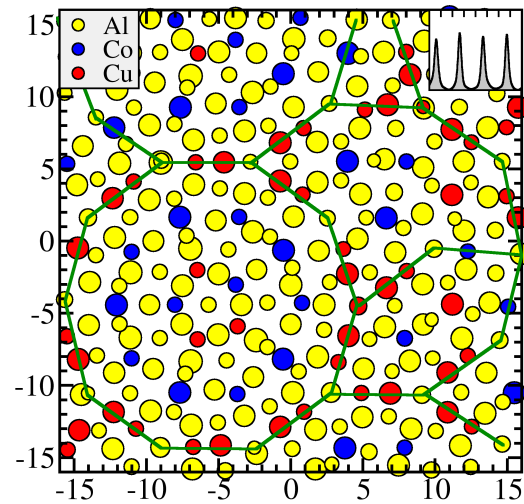
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Atomic structures of Al-Co-Cu decagonal quasicrystals (QCs) are investigated using empirical oscillating pair potentials (EOPP) in replica exchange molecular dynamic (MD) simulations that we enhance by Monte Carlo (MC) swapping of chemical species. Predicted structures exhibit planar aperiodic decagonal tiling patterns, and either 4 or 8 Å periodicity along the perpendicular direction. We then recalculate the energies of promising structures using first-principles density functional theory (DFT), along with energies of competing phases. Although we find that our  $\tau$ -inflated sequence of QC approximants are energetically unstable at low temperature by at least 8 meV/atom, we extend our study to finite temperatures by calculating harmonic vibrational entropy as well as anharmonic contributions that include chemical species swaps and tile flips. Our results suggest that the Al-Co-Cu quasicrystal phase is entropically stabilized above temperatures in the range 600-800K, and that it decomposes into ordinary (though complex) crystal phases at low temperatures, including a partially disordered B2-type phase. Finally, we discuss the influence of density and composition on QC phase stability, and we compare the structural differences between Co-rich and Cu-rich quasicrystals.

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**Fig.1:** Simulated Co-rich structure. 4.7 Å tiling outlines pentagonal bipyramid motifs. Inset shows alternation of flat and puckered layers with net 8 Å vertical periodicity.



**Fig.2:** Simulated Cu-rich structure. 6.2 Å tiling outlines hexagon, boat and 20 Å "Burkov decagon". Inset shows no alternation of layers with net 4 Å vertical periodicity.

## Formation enthalpies of Al-Mn-Pd and the structure of the *i*-AlMnPd quasicrystal

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We evaluate from first principles formation enthalpies of phases in the Al-Mn-Pd ternary alloy system, taking into account all crystal structures as reported in the assessed phase diagrams of the ternary and its binary alloy subsystems (Al-Mn, Al-Pd, and Mn-Pd), as well as additional reported or hypothetical structures [1]. We propose several corrections of the current Al-Mn binary diagram, including proposal for previously unreported low-temperature stable AlMn<sub>2</sub> phase. In the ternary Al-Mn-Pd system, we find an icosahedral approximant with 552 atoms/cell spontaneously formed in atomistic simulations to be stable down to zero K temperature, and even larger 2338-atom approximant to be unstable by mere 4 meV/atom. The structure building blocks of these approximants, presumably shared with icosahedral phase, are pseudo-Mackay clusters, and Al<sub>12</sub>Pd icosahedra. We discuss the discovered icosahedral structure in the context of the preexisting established models: 6D Katz-Gratias [2], Quandt&Elser [3], and also experimentally observed structure in AlPdCrFe system based on the same building blocks [4], plus the Henley's canonical-cells tiling geometry [5].

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## What is the origin of the difference between aluminum and boron icosahedral clusters and cluster solids?

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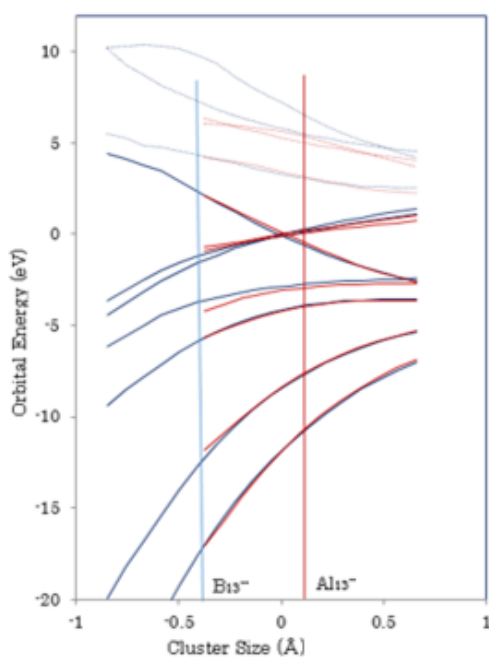
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Boron (B) and aluminum (Al) belong to the same group 13 in the periodic table and are next to each other, so the size dependence of the cluster orbital energies of the same cluster structure have similar shapes. By adjusting the energy and size, they overlap very well as shown in Fig.1 [1]. Fig. 1 is for a 13 atoms icosahedral cluster with a central atom, and only the size of the stable cluster is different (two vertical lines). Because HOMOs are bonding and antibonding orbitals for Al and B, the cluster structures are stable and unstable, respectively. The origin of these is considered to be that in B, there is no 1p orbital below the 2p orbital, so the 2p and 2s orbitals are almost the same size, whereas in Al, there is a 2p orbital below the 3p orbital, so the 3p orbital is larger than the 3s orbital.

On the other hand, in icosahedral cluster solids, the B systems (approximants) is a semiconductor and is difficult to metalize due to self-compensation [2]. In the Al systems (quasicrystals and approximants), several dozen phases, except for Al-Ru-Si 1/0-approximants [3], are all metals and are difficult to become semiconductors [4]. What is the origin of this difference?

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**Fig.1:** Cluster size dependences of orbital energies for  $B_{13}^-$  (blue line) and  $Al_{13}^-$  (red line) icosahedral clusters. Two axes are normalized, that is, energy and size axes for B are reduced and expanded, respectively, as the cross points between 1fb and 2p orbitals coincide at the same position and each line overlaps as much as possible. Vertical lines show the most stable size of  $B_{13}^-$  and  $Al_{13}^-$  [1].

## Magnetism in CoFeNi-based high-entropy alloys: From basic scientific questions to applications

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High-entropy alloys, HEAs [1] are metallic systems composed of 4, 5 or more principal elements in equimolar or near-equimolar concentrations, where a solid solution on a simple lattice (bcc, fcc, hcp) is stabilized as the only or the main phase in the material. The aim of this contribution will be to highlight both the basic-science as well as the applied side of these alloys.

Our experimental investigations into the Co-Cr-Fe-Mn-Ni high-entropy alloy [2] were conducted on a high-quality non-equiatom material grown by the Czochralski method. As the material is homogenous on the microscale (SEM elemental mapping) and sufficiently homogenous on the nanoscale without short-range ordering (APT, HAADF STEM and EELS), it can be taken to be a prototype of an “ideal” high-entropy alloy – one where a single solid solution with no deviations from complete randomness is present. From the viewpoint of magnetism, we are dealing with an unusual system, which is at the same time random, contains several types of magnetic moments, is a concentrated magnetic system (all the elements are magnetic) and is frustrated (contains both AFM and FM interactions). Instead of long-range magnetic order, a spin freezing transition occurs at  $T_f \approx 20$  K to a spin-glass-like state. In this asperomagnetic state, the system is non-ergodic, which can be demonstrated by zfc-fc susceptibility splitting, shift of the cusp in AC susceptibility with frequency, ultra-slow decay of thermoremanent magnetization or the thermal memory effect.

In contrast, the AlCoFeNiCu<sub>x</sub> ( $x = 0.6-3.0$ ) series of high-entropy alloys [3] is far from “ideal” HEAs as the samples exhibit both nanostructure as well as a multiphase microstructure. The materials belong to a subclass of high-entropy alloys [4], which might find potential applications as soft-magnetic materials in low-frequency AC applications such as transformers. At  $x = 2.0$ , the alloy exhibits a low coercivity of 650 A m<sup>-1</sup>, a decent saturation polarization of 0.55 T, as well as zero magnetostriction  $\lambda_s = 0$ . The zero magnetostriction is a consequence of the three-phase microstructure and could in the future lead to »supersilent« soft-magnetic materials – materials which could be used at 50 or 60 Hz without emitting annoying humming sounds.

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## Deep learning enables identification of a previously unknown icosahedral quasicrystal from multiphase powder diffraction patterns

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Since the first discovery of a quasicrystal by Shechtman *et al.* [1], approximately 100 stable quasicrystals have been identified [2,3]. While transmission electron microscopy is a powerful tool to determine the existence of quasicrystal phases, the experiment is much more time- and effort-consuming than powder x-ray diffraction, which is rapid as well as automatic. To facilitate the search for novel quasicrystals, it is thus desired to establish a reliable phase-identification technique from powder patterns even if the quasicrystals exist in the form of multiphase mixtures. In this study, we successfully identified a previously unknown Al–Si–Ru icosahedral quasicrystal from multiphase powder patterns using deep learning technologies. Deep learning models were trained using artificially generated powder diffraction patterns of multiphase mixtures and could determine the presence/absence of icosahedral phases with an accuracy greater than 92% from the actual powder patterns. Using this trained model, we screened 440 powder patterns accumulated in the laboratory, leading to the discovery of the new icosahedral quasicrystal.

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