Online supplementary information for "Cluster packing geometry for Al-based F-type icosahedral alloys"

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The structure refinement of the new approximant crystal is supplemented with further evidence.

1. High resolution powder X-ray diffraction

The present work details a crystal structure determined and refined using single crystal X-ray diffraction. The reader might well consider that the reliability indices of $R(F) = 11.96(\%)$ and $R_w(F) = 12.13(\%)$ are not sufficiently low for these indices are usually expected to be well below 10% for an ordinary crystal structure analysis of an intermetallic compound. In fact, we can further reduce these values to slightly below 10 % by introducing vacancies and additional splitting positions within the inner shell of M-clusters, in which atomic arrangements are likely to be weakly disordered. This attempt however causes an even more unfavorable situation in other parts of the structure; that is, the atomic displacement parameters would become negative for some of the atoms. It seems that the present diffraction dataset is still insufficient to perform such kind of analysis, which necessarily increases the number of parameters to be refined.

In order to increase the credibility of our refinement, we have performed a high-resolution powder X-ray diffraction measurement with synchrotron radiation. For this experiment, a single phase sample with a nominal composition of $Al_{69.4}Pd_{22.3}Cr_{2.2}Fe_{6.1}$ was prepared through annealing at 850°C for 4 days. A high-resolution powder X-ray diffraction measurement was performed at the SPring-8 synchrotron radiation facility (Harima, Japan). In Figure 16, the resulting diffraction profile is shown along with a simulated diffraction pattern calculated from the refined structure. The JANA2006 software package (Petricek *et al.*, 2006) was used for the simulation. A striking resemblance between the measured and simulated patterns can be observed.

2. Structure analysis using only main reflections

In Subsection §§5.2 it is argued that the crystal structure reported by Sugiyama *et al.* (1998) represents what it looks like if eight half-translates of the true structure is superposed, based on the speculation that their diffraction measurement may have failed to detect the superlattice reflections. In order to add some more credibility to the argument, here we recur to structure analysis (Subsection §§3.2) using only the main reflections in the diffraction data. The aim of this analysis is to examine if the two kinds of cluster reported by Sugiyama *et al.* (1998) show up through such an analysis, thereby to verify our hypothesis on Sugiyama's measurement. However, any strive to obtain an accurate structure solution from such an incomplete dataset is senseless. Hence, we will only obtain a preliminary estimate of the structure through direct method (the charge flipping algorithm, in this case).

A dataet is prepared in the following way: First, all the reflection intensities with at least one odd Miller indices are removed from the same dataset as the one used in Subsection §§3.2. The Miller indices for the remains are simply halved, so that the dataset can be analyzed assuming the primitive cubic crystal with a lattice constant of 20.27Å. The space group is readily identified to be $Pm\bar{3}$ and the symmetry averaging is performed resulting in 1536 independent reflections satisfying $I > 3\sigma(I)$ with $R_{int} = 5.40\%$. Then the *superflip* program is run several times, and the most reasonable estimate of the charge density map is adopted. An initial structure model is obtained via the automated peak-search algorithm of JANA2006. Finally a single least-squares fitting is performed to refine the atomic positions as well as the atomic displacement parameters. The reliability indices are $R(F) = 26.80(\%)$ and $R_w(F) = 30.23(\%)$.

Centered at the vertex (Wyckoff, 1a) and the body center (1b) of the cubic unit cell, two kinds of cluster resembling those reported by Sugiyama *et al.* (1998) are clearly observed. Their shell structures are depicted in Figures 17 and 18.

References

Momma, K. & Izumi, F. (2008). *J. Appl. Crystallogr.* **41**, 653–658.
Petricek, V., Dusek, M. & Palatinus, L., (2006). Jana2006. the crystallographic computing system. http://jana.fzu.cz/ Institute of Physics, Praha, Czech Republic.
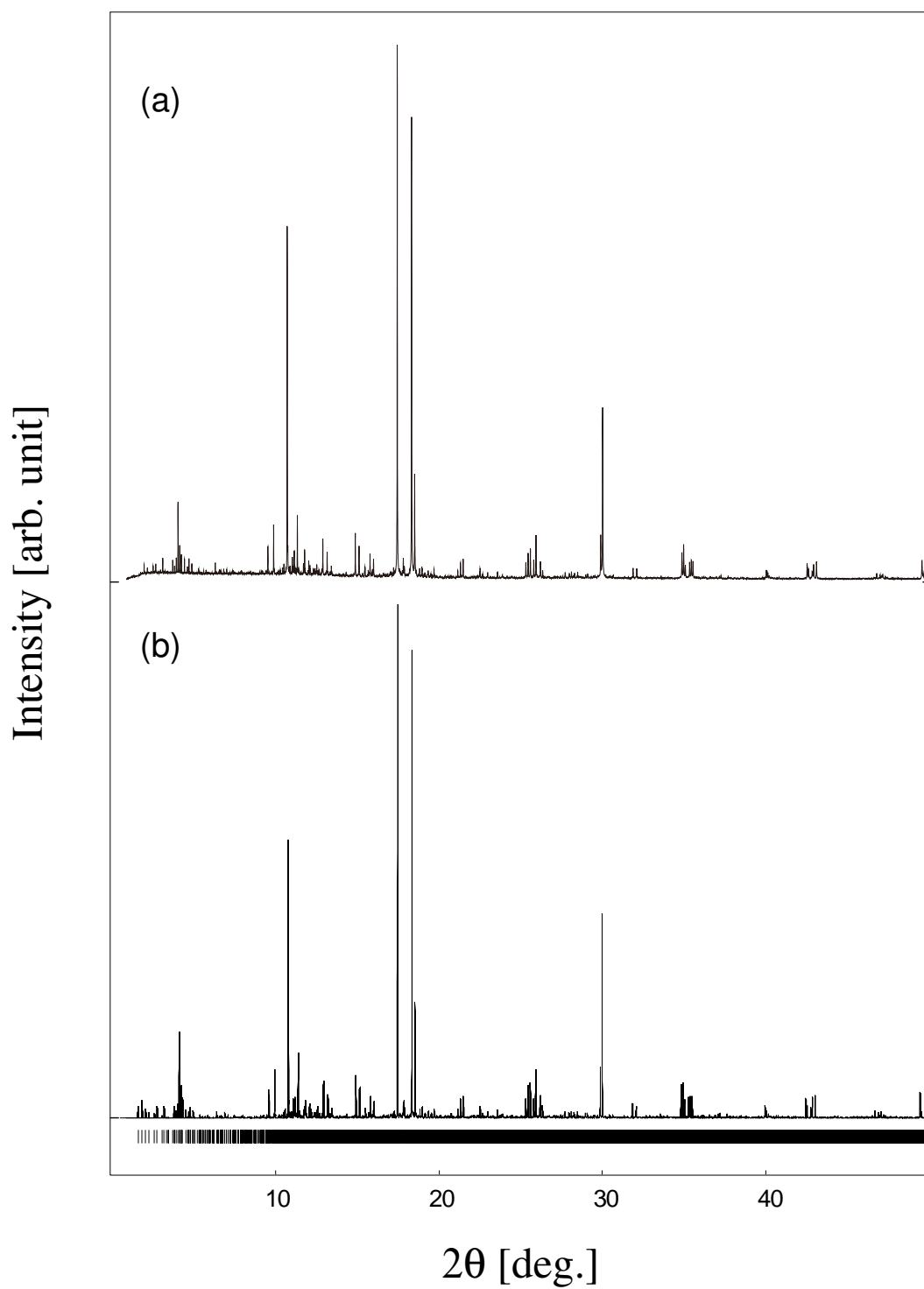Sugiyama, K., Kaji, N., Hiraga, K. & Ishimasa, T. (1998). *Z. Kristallogr.* **213**, 90–95.

Figure 16

(a) A powder X-ray diffraction pattern measured with synchrotron radiation (wave length, 0.65285Å) and (b) one simulated with the refined structure parameters given in Appendix §B. In (b), the calculated peak positions are indicated with vertical bars.
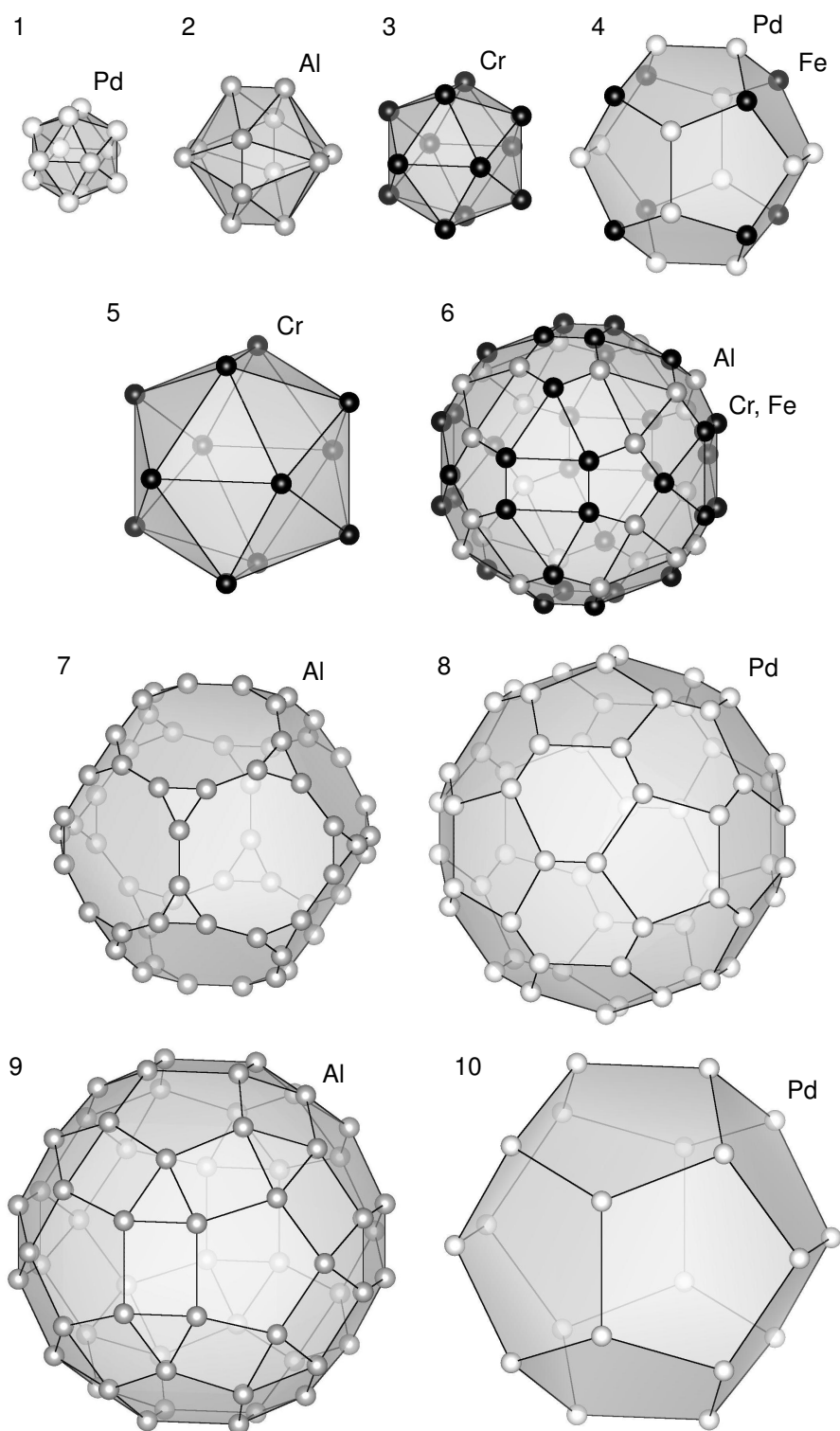
Figure 17

Ten shells centered at the vertex of the unit cell. Except the shell No.2, they have the icosahedral symmetry in shape. The No.2 appears to be a dodecahedron, but some of the vertices are missing. These shells compare nicely to the shell structures of the main cluster reported by Sugiyama *et al.* (1998); however, due to the roughness of the present analysis, three shells with Al atoms are missing here. The average radii of the ten shells are (No.1) 2.88Å, (2) 4.24Å, (3) 4.55Å, (4) 6.68Å, (5) 7.33Å, (6) 8.23Å, (7) 8.86Å, (8) 10.25Å, (9) 10.69Å and (10) 10.84Å.
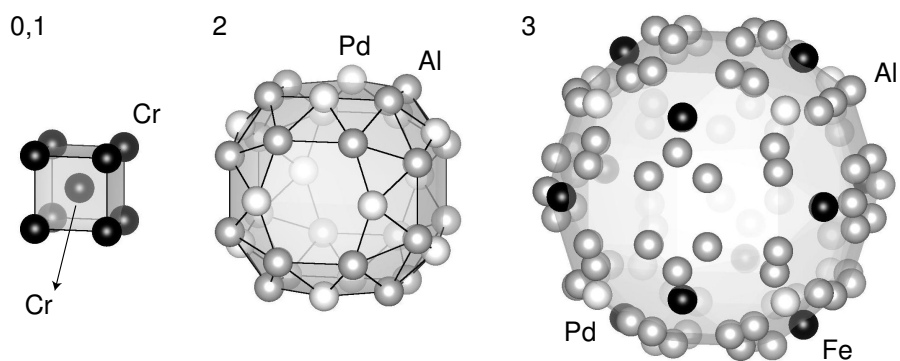
Figure 18
A few shells centered at the body center of the unit cell. Note that there is an atom in the center. The icosahedral symmetry is strongly broken already in shape, and the shape is in reasonable agreement with that of the second cluster reported by Sugiyama *et al.* (1998). Some of the light Al atoms are absent here. The average radii of the shells are (No.1) 2.56Å, (2) 4.78Å and (3) 6.64Å.