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Experiment Report Form

	Experiment title: Short range order in the disordered *fcc* lattice of the $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ high entropy alloy	**Experiment number**: 08-01 1063
Beamline: BM08-LISA	**Date of experiment**: from: August 24, 2018 to: August 28, 2018	**Date of report**: 01.03.2020
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Report taken partly from available pre-print:

Fantin, Andrea and Lepore, Giovanni Orazio and Manzoni, Anna M. and Kasatikov, Sergey and Scherb, Tobias and Huthwelker, Thomas and d'Acapito, Francesco and Schumacher, Gerhard, Short-Range Chemical Order and Local Lattice Distortion in a Compositionally Complex Al $_8$Cr $_{17}$Co $_{17}$Cu $_8$Fe $_{17}$Ni $_{33}$ Alloy. Pre-print available at SSRN: https://ssrn.com/abstract=3509325

Abstract:

This work presents an X-ray absorption spectroscopy study on a single-phase state of the $Al_8Cr_{17}Co_{17}Cu_8Fe_{17}Ni_{33}$ compositionally complex alloy (CCA), focused on the local crystal structure around each alloying element. The comparison of 1st shell bond lengths, obtained by the analysis of extended X-ray absorption fine structure (EXAFS) measured at the K-edges of each alloying element, indicates that $Al_8Cr_{17}Co_{17}Cu_8Fe_{17}Ni_{33}$ crystallizes in a slightly distorted arrangement of an fcc lattice. A modest V-shaped bond length dependence of the alloying elements with increasing atomic number is observed, with minima and maxima at Cr/Co, and Al/Cu, respectively. 1st shell bond lengths range over ~0.03 Å, potentially giving rise to lattice distortions of ~0.04 Å. EXAFS results clearly indicate short-range order in the alloy: pairing of Al with Ni and Cu is favored, correlating well with a γ' precipitate composition (Al-Ni-Cu rich) reported in previous work, while Al-Cr bonding is unfavored and no Al-Al pairs are observed. Electronic structure information was obtained through comparison between near-edge regions of alloying elements and corresponding pure metals. Energy shifts and intensity comparison of K-edge features agree with a slight charge variation of *p* states in $Al_8Cr_{17}Co_{17}Cu_8Fe_{17}Ni_{33}$, where Ni and Cu act as *p* states electron acceptors in the alloy.

Relevant figures:

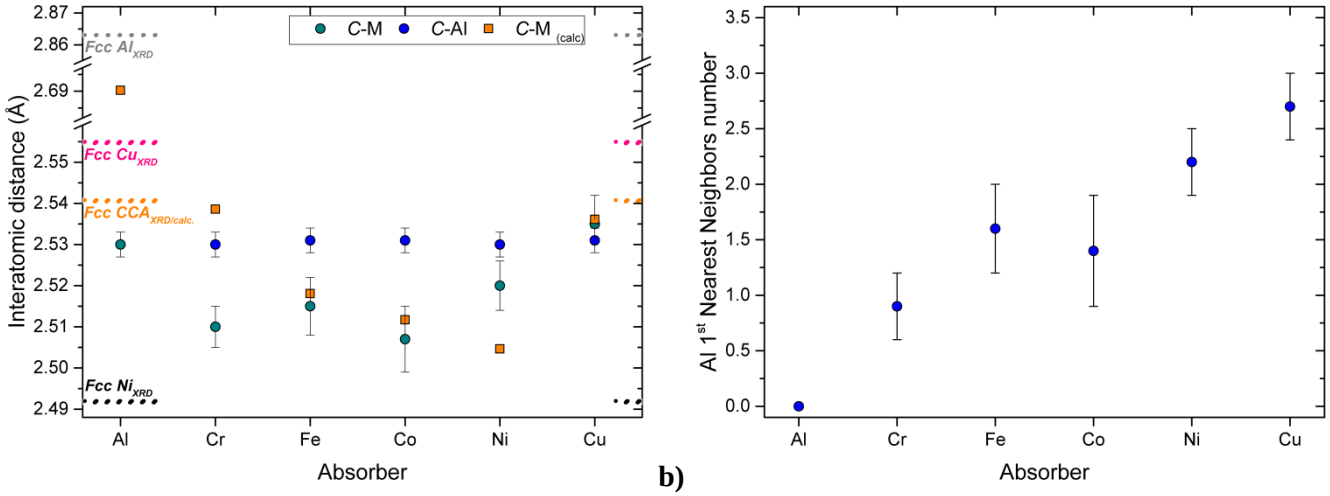

Figure 1. **a)** Interatomic distances in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ between each investigated element Al, Co, Cr, Cu, Fe and Ni and the average *3d* absorber (dark cyan symbols) and Al (blue symbols). Orange symbols (*C*-$M_{(calc)}$) are calculated distances obtained by summing each absorber's metallic radius with the weighted average radius of *3d* metals in the alloy (according to stoichiometry), therefore representing the expected *C*-M distance assuming a completely disordered distribution of 3d metals. Grey, purple and black dashed lines represent average interatomic distances derived from XRD literature data for pure *fcc* Al, Cu and Ni, respectively; the orange dashed line represent both the average CCA interatomic distances, obtained from XRD data, and derived from metallic radii given in Greenwood and Earnshaw (Chemistry of the Elements. *Elsevier Science*, 2012). All XRD data refer to room temperature acquisitions. **b)** Number of Al 1st nearest neighbors around each investigated element in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$.

Main results and short discussion:

Discrepancies in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ between average bond distances calculated from the unit cell obtained by X-ray diffraction (orange dashed line), and local environment results obtained by EXAFS (blue and dark cyan symbols), arise, as highlighted in Figure 1a. In addition, expected local distances, calculated on the basis of a completely disordered distribution of 3d metals in the alloy (orange symbols) match only partially with EXAFS results. These findings are rationalized by assuming slightly distorted *fcc* unit cells with preferred chemical ordering, as clearly demonstrated for Al in Fig. 1b.

The 1 st shell average distances of each alloying element range in an interval of ~0.03 thus resulting in a maximum possible lattice distortions in the *fcc* unit cell of ~0.04 Å. These values are much smaller than those predicted solely by atomic radii considerations. The Al metallic radius in the CCA is estimated to be of the same order than the average TM one, i.e. 1.26 Å, shorter by about 0.17 Å than the tabulated value of 1.43 Å of pure Al. Al reduces its metallic radius in order to accommodate into the lattice, lessening its distortion. The Al size decrease upon alloying is ascribed to Al-*p* states hybridization with transition metal *sp/d* orbitals. Large discrepancies between experimental interatomic distances and predictions based on metallic radii were observed for Cr and Ni, suggesting the occurrence of further local chemical Ni ordering with Cr atoms. Indeed, the discrepancies between the different radii of *3d* metals, i.e. Cr and Ni, and the accommodation of these discrepancies seem to be the main actors inducing lattice distortions. Finally, the Al-Ni/Cu short-range order found in the single-phase region of the investigated CCA $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ correlates with the Al-Ni-Cu based γ' precipitation composition appearing below 900 °C. This correlation is particularly interesting as it extends possible applications of XAS in getting information on the origin of precipitates in materials showing complex phase diagrams, by studying them in their respective single-phase states.

Summary:

Two important points in the characterization of HEAs, namely local chemical ordering and local lattice distortions, were clarified by means of a local XAS approach during the beamtime allocated, providing a tool to answer the open questions reported in recent reviews on High-Entropy Materials (*cf.* e.g. George EP *et al.*, High-entropy alloys. *Nature Reviews Materials* 2019;4:515). EXAFS analysis identified local distortions in $Al_8Co_{17}Cr_{17}Cu_8Fe_{17}Ni_{33}$ (less than ~0.04 Å in an unit cell of 3.59 Å) and a higher affinity of Al for heavier *3d* metals, with Cu-Al being the preferred pair.