



	Experiment title: Structure of thiolate-capped Ag nanoparticles by total scattering x-ray diffraction	Experiment number: HS-4543
Beamline: ID31	Date of experiment: from: 11 nov 2011 to: 14 nov 2011	Date of report: 28/08/2013
Shifts: 8	Local contact(s): Andy Fitch	<i>Received at ESRF:</i>
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Report:

Au and Ag nanoparticles (NP) capped with alkanethiolate or alkanedithiolate molecules have shown permanent magnetism while the bulks, as metals, are diamagnetic [1]. The origin of this magnetism is probably related to the finite particle size and to the interaction of the surface metal atoms with the ligand. In order to verify this hypothesis, a fine control of the constitution, size, shape and surface of the nanoparticles is required. In particular, the crystallographic structure is essential to correlate the nanoparticles structural and electronic properties to their magnetic moment. In order to provide structural information complementary to previous XAFS measurements [2] and to explore the way the dodecanethiolate binds and interacts with the Ag surface, we proposed this experiment to measure the total diffuse scattering and evaluate the atomic pair distribution function (PDF) of x-ray scattering data.

The experiment was performed on ID31, at 50keV, corresponding to a wavelength $\lambda = 0.248\text{\AA}$.

0.5 mm glass capillaries were filled with powder samples and 2θ scans in the range $1^\circ < 2\theta < 124^\circ$ were performed. The PDF data $G(r)$ were obtained utilizing the PDFgetX2 software [3], the modelling was carried out using the PDFgui package [4]

We measured 5 samples under the same experimental conditions; they differ for the capping agents and for NP sizes: two dodecanethiolate-capped Ag NP samples with sizes of about 4 – 5 nm, three phenylethanethiolate-capped Ag NP with sizes in the range 6 – 17 nm. Moreover, a sixth sample of bulk Ag was measured as a reference to which compare the corresponding NP data.

Fig. 1 (a –f) shows the $G(r)$, the fits of the samples and the difference between experimental and calculated data; in table 1 the final values from the refinements are reported.

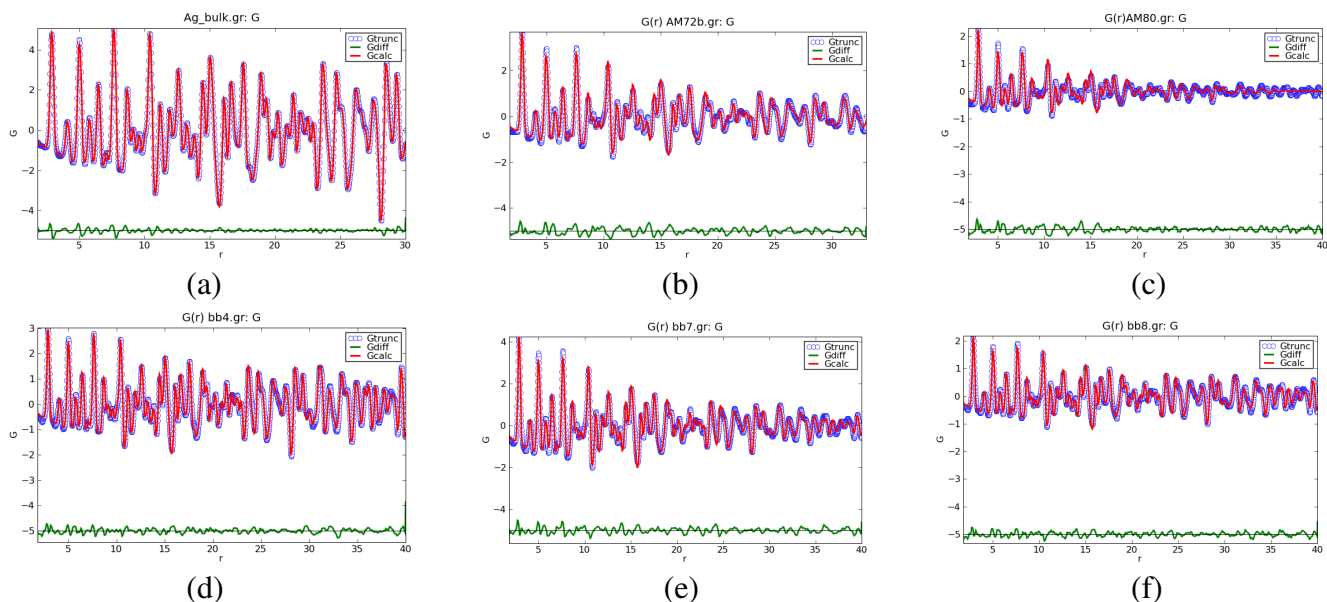


Fig 1 G(r) plot of: (a) bulk Ag; (b) 6 nm dodecanethiolate-capped Ag NP; (c) 4 nm dodecanethiolate-capped Ag NP; (d) 17 nm phenylethanethiolate -capped Ag NP; (e) 6 nm phenylethanethiolate -capped Ag NP; (f) 9 nm phenylethanethiolate -capped Ag NP.

	(a)	(b)	(c)	(d)	(e)	(f)
a (Å)	4.0858(6)	4.085(2)	4.082(5)	4.0872(9)	4.086(1)	4.087(2)
u_{iso} (Å ²)	0.0130(4)	0.015(1)	0.018(3)	0.0141(9)	0.016(1)	0.015(2)
NP diameter (nm)		6(1)	4(1)	17(4)	6(1)	9(1)
R_w (%)	6	17	26	12	16	17
Ag-Ag bond (Å)	2.8891(4)	2.889(1)	2.886(3)	2.8900(6)	2.8891(9)	2.889(1)

Table 1 Structural parameters obtained from PDF refinements for the samples: (a) bulk Ag; (b) 6 nm dodecanethiolate-capped Ag NP; (c) 4 nm dodecanethiolate-capped Ag NP; (d) 17 nm phenylethanethiolate -capped Ag NP; (e) 6 nm phenylethanethiolate -capped Ag NP; (f) 9 nm phenylethanethiolate -capped Ag NP.

No significant differences among the samples were found as a function of the particle size or of the capping agent; Ag-Ag bond lengths (first neighbor) are similar and comparable with the bulk one. This result is in agreement with the literature [5] that predicts the presence of significant strain only in NP smaller than 5nm. In our case the sizes reported in table 1 are in good agreement with those determined by STEM and TEM measurements [private communication], but they are probably not so small to detect lattice contraction and bond lengths differences. In the refinements we tested the presence of non crystallographic structures, i.e. cuboctahedral, icosahedral and dodecahedral structures, typical of fcc noble metal particles [6] but no evidence of such features was found. The refinements were performed using either the Ag cubic (fcc) structure and a mixture of cubic and hexagonal (hcp) structure. The coexistence of the two Ag phases was reported in the literature [7] for coated Ag NP. In that paper a phase separation within the single grain was reported and possibly correlated to the capping agent. We checked for the presence of both fcc and hcp phases in a single Ag grain but such phase separation was not found.

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