Supporting information

Preparation of TEM/EELS samples

The TEM samples were prepared by drop-casting the ferrimagnetic HFn onto standard holey carbon support films (Agar Scientific Ltd) under anaerobic conditions. As soon as the sample was naturally dried, it was put into the microscope.

Quantification by EELS

As mentioned in the main text, two spectrum images were acquired from the zone to be analysed, one from the core-loss range (CLSI) and one from the low-loss range (LLSI). In fact, specimen drift during the several minutes required to record the CLSI means that the areas covered in the two SIs are not identical. A box of pixels is therefore defined around each particle to be analysed (64 particles which were fully present in both SIs) the boxes being composed of the same number of pixels in both SIs but not necessarily exactly the same shape because of the drift-induced distortions. The spectra are then summed in these boxes and the resulting two spectra are spliced together by normalising them in a region (150 to 200 eV) which is present in both the CLSI and the LLSI.

It was found that when summing over a fairly large number of pixels in zones lying between particles a small iron signal was still detectable, corresponding to about 15 atoms.nm^2. The results for the particles were therefore corrected by subtracting the appropriate number of atoms for the area analysed. The accuracy of the results depends on a number of factors. Both systematic and statistical sources of error exist. In EELS quantification in general systematic errors may in principle arise from 1: incorrect camera readout and dark-current noise subtraction, 2: incorrect camera gain-variation compensation, 3: inadvertent camera saturation at the zero-loss peak, 4: incorrect measurement of convergence and collection angles, 5: inaccuracies in the calculated cross-sections, 6: the effects of multiple inelastic scattering, 7: an incorrect background-subtraction model and 8: imperfect correspondence between the zones examined in the CLSI and the LLSI. For points 1 to 4, great care was taken to measure all the appropriate parameters as accurately as possible and not to saturate the camera (see above) and we believe should not produce a cumulative error greater than 5%. The cross-sections themselves are in long-established general use and the Fe-L edge is considered to be accurate to within ±10% (Egerton, 1993). Multiple scattering is here considered negligible (after Fourier-log deconvolution of the spectrum, the number of counts under the edge decreases by about 2%, an effect which is compensated by using the whole low-loss region as the incident intensity I_{ll} in equation (2). The background subtraction model can be shown to give an estimate of the background integral (over ranges similar to those used here) which is accurate to within less than one percent in low-noise data (1).   Figure A shows a typical spectrum from a particle after background subtraction (green curve) and the associated cross-section normalised to give the same area under the integrated region (blue curve). The two curves can be seen to be converging (within the limits of the statistics) after about 750-760 eV, indicating that the integration window of 70 eV is sufficient.

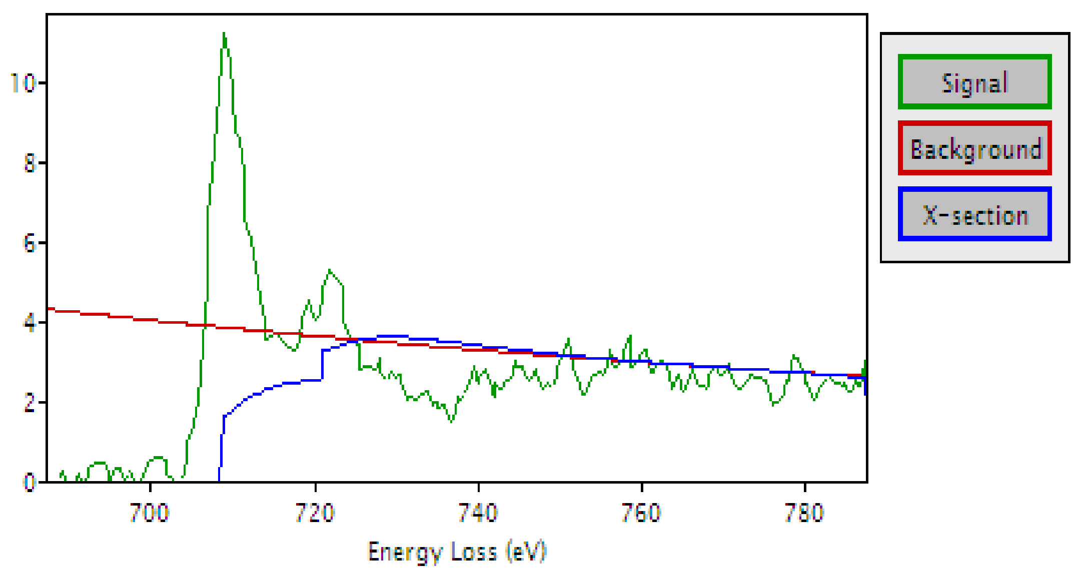

Figure A. Typical spectrum from particle and calculated H-S Cross-section

Points 1 to 7 may thus produce a total error margin of around 12% when added in quadrature. The contribution of the final point has been determined empirically. For a given particle, the same number of pixels were always integrated in the LLSI and CLSI (the brightest ones). Exchanging up to three (in the bigger particles, one or two in the smaller ones) of the pixels chosen to be included/excluded at the particle periphery changes the result of the analysis by up to 8%.

Statistical errors arise in both the background and signal estimations. These are dealt with in the standard way and lead to Poisson-type errors ($n^{1/2}$) in the total counts in the integrated region (n) and somewhat larger error in the background-subtraction fit and its extrapolation. It can be shown (Egerton, 2011) that the combined relative error for the combination of these effects is given by the formula

$$e_{Fe} = I_{Fe}/(I_{Fe}\, h.I_b)^{1/2}$$

Where I_b is the integral under the background fitting region and h is a constant which varies as a function of the relative widths of fitting and background windows, and which is equal to about 14 for approximately equal widths, as used here. The main source of statistical error is thus the background extrapolation. The values of e_{Fe} for our data vary from point to point but lie in the range 0.05-0.015 or ± 5-15%.

Only the statistical errors and those arising from point 8 in the systematic errors will produce scatter in the data. The error bars shown thus represent the sum in quadrature of these two contributions. However, the slope of the curve may be affected by the systematic errors. When all their sources are added in quadrature and the result combined with the error arising from the "scatter producing" errors, the value for the slope of the curve should be correct to 15% (65% confidence limit).

HAADF quantification

The particles are found and counted automatically by a thresholding routine in the programme Digital Micrograph (Gatan Inc) which ascribes only pixels above a certain intensity (set by the user) to be included in the particles. A potential error arises from the threshold intensity chosen, which by visual inspection in our image might reasonably be varied over a range corresponding to at most 1or occasionally 2 more (or less) pixels being included around the edge of the particle, leading to an error δr in the radius of the particles of about ± 0.2 nm (This fits quite well with the probe size of around 0.5 nm). This in turn will give an error margin in the measured volume of $4\pi r^2 \delta r$ or $4A\delta r$, which converts to a relative error in the volume of $3\delta r/r$, or of the order of 15% for the bigger particles (r > 7nm) and up to nearly 50% for the smallest. These errors should however be essentially systematic, since the same threshold is used on all particles and pixel to pixel statistical errors (of the order of 1% for this not very noisy image) will tend to be averaged out going around the periphery of the particle. They can thus produce an error in the slope of figure 6 but should not introduce scatter. We were reassured to find that picking the most visually correct threshold which seemed to select the entire particles but no unnecessary exterior pixels yielded the curve with the slope rather close to 1 seen in the figure.

1. Egerton, R. F. (1996) *Electron energy-loss spectroscopy in the electron microscope*, Springer

2. Egerton, R. F. (1993**)** *Ultramicroscopy*, *50*, 13-28