

# Au Bonding and Ferromagnetism in Thiol-capped Au Nanoparticles

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The <sup>197</sup>Au Mössbauer parameters of the magnetically ordered subspectrum of thiol-capped Au nanoparticles are interpreted in terms of the bonding internally to metal atoms and externally to sulphur atoms. It is proposed that ferromagnetism in these nanoparticles only occurs while they are in the size regime which allows Marks decahedra to be stable and disappears as soon as they change to the FCC structure of bulk Au.

## 1. Introduction

The development of nanoscale materials has produced many strange effects and we are now used to the concept that the properties of nanomaterials may be considerably different from those of their bulk partners. However, the discovery that thiol-capped Au nanoparticles were ferromagnetic [1,2], not just at low temperatures, but up to room temperature, must rank as one of the more surprising. To add to this, we have recently shown [3] that thiol-capped Ag and Cu nanoparticles are also ferromagnetic over these temperatures.

The discovery raises many questions about the mechanisms. What is the origin of the moment? What is the origin of the ferromagnetic coupling? Even more intriguing is that fact that the hysteresis loop changes little up to room temperature, indicating an extrapolated Curie temperature of about 1000 K. Furthermore, the 2 nm particles are not superparamagnetic at room temperature, by far the smallest particles with this property. This makes them the ferromagnets with the highest anisotropy, approximately 100 times that of SmCo<sub>5</sub>. Also intriguing is the critical dependence on size – the ferromagnetism disappears between 2 nm and 3 nm.

## 2. Experimental

The Au nanoparticles were made by the method of Brust et al. [4] using dodecanthiol as the organic capping to limit the particle size. We have taken measurements with SQUID magnetometry, XMCD, <sup>197</sup>Au Mössbauer spectroscopy and TEM in order to characterise these nanoparticles [3]. It is principally the Mössbauer measurements which we wish to address here and the details of the remainder may be found in [3].

## 3. Results

The <sup>197</sup>Au Mössbauer spectrum of the Au nanoparticles at 5 K is shown in Fig. 1. The main contribution is a single line centred at an isomer shift (IS) of -0.26 mm/s w.r.t. Au metal, and a width of 2.0 mm/s, very close to the narrowest achievable. This is from the metallic core of the nanoparticles. The second component is from the surface gold atoms and is split by both the electric quadrupole interaction and magnetic dipole splitting. The IS is 3.55 mm/s, the quadrupole splitting (QS) is -4.3 mm/s and the magnetic hyperfine field 9.0 T. This is the first time that a hyperfine field has been observed due to a magnetic moment resident on a gold atom. Previous magnetic splittings in gold alloys have been due to a transferred hyperfine field from a ferromagnetic 3d element. Comparing the saturation magnetization to the estimated number of surface Au atoms, gives an average moment of 0.3  $\mu_B$ /magnetic Au atom. Relating this to the hyperfine field, gives a value of 30 T/spin which may be compared with the well known value of 11 T/spin for Fe.

The systematics of the correlation of the QS  $\sim$  IS in gold compounds are well understood [5]. Fig. 2 shows the bands of observed values for Au(I) and Au(III) compounds, modified from [5]. Because Au(I) atoms have 6s-6p hybridization, this leads to linear bonding with the two bonds being 180° apart. The QS must be negative. Au(III) has  $sp^2$  bonding, which leads to square planar bonding and a positive QS. In the absence of either an internal or an applied magnetic field, the sign of the QS cannot be determined experimentally and so it is commonly inferred for the majority of Au compounds. Au metal has zero QS, since it is FCC, and it is also the reference for the IS, so it is at (0, 0).

The nearest comparable Au material which has been measured previously by Mössbauer spectroscopy is the Au<sub>55</sub> molecule. This is also stabilized by capping it so that there are four distinguishable types of Au atoms, being the core, and surface atoms on the corners, edges and faces, each with different bonding. The parameters of these are all marked on Fig. 2, together with the parameters for our AuSR nanoparticles.

#### 4. Discussion

We are now in a position to discuss the bonding of Au atoms in Au nanoparticles. The parameters of the core atoms are the same as those of the Au<sub>55</sub> core. The isomer shift is negative due to a small lattice expansion in these nanoparticles. The magnetic fraction of the spectrum represents 40% of the total, but after correction for the different recoilless fractions, this comes up to 53%, reasonably close to the 63% of the atoms expected to be on the surface for a three shell structure.

It has been shown [6] that, on a flat surface, each SR molecule occupies an area of 21.4 Å<sup>2</sup>. If we assume that this also applies to these nanoparticles, and approximate the shape to a three shell cuboctahedron, then we find that it should have 28 SR molecules for 92 surface Au atoms, giving a ratio of 30%, in exact agreement with the chemical decomposition.

However, it has been shown recently that nanoparticles often adopt different structures to those which occur in the bulk [7-9]. Common alternative structures are icosahedra and Marks decahedra, both of which have 5-fold symmetry. This can be accommodated in very small particles by distortion and strain, but cannot be maintained in the bulk. It has been shown experimentally recently [10] that an Au nanoparticle with 102 atoms is a Marks decahedron.

In interpreting the Mössbauer parameters for the surface atoms, the situation does not fit nicely into the bands which make up Fig. 2. The surface gold atoms have a full gold bonding on the inside and sulphur bonding on the outside. So it is neither metallic, nor an insulator. If we start from the parameters for Au metal, then the origin of the ferromagnetic moment has been attributed to a partial d-hole. This would have the effect of decreasing the shielding of the s-electrons, hence increasing the IS as observed. The change of 4 mm/s

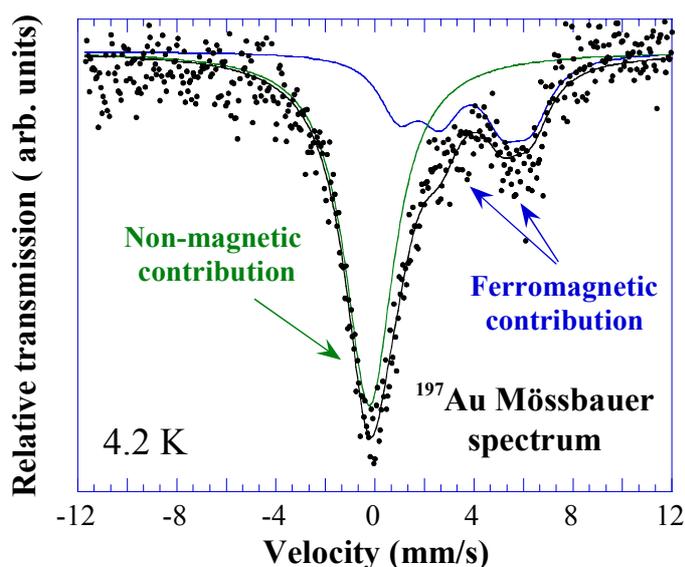


Fig. 1. <sup>197</sup>Au Mössbauer spectrum of the AuSR nanoparticles, taken at 5 K.

would correspond to 0.5 of a d-electron. A QS will clearly be generated since the atoms are no longer in a cubic environment. If we compare the situation to a Au(I) with two sulphur bonds, then there will clearly be a reduction in the QS compared to the Au(I) band in Fig. 2, because of the increased symmetry on the metallic neighbours inside.

The geometry of the sulphur bonding is not entirely clear. It has been shown [6] from calculations of alkanethiolates on Au surfaces, that the sulphur atoms are not positioned directly above a particular Au atom, as would be expected for 6s-6p bonding, but are nestled in the hollows between Au atoms in both the (100) and (111) planes. This bonding has both  $\sigma$  and  $\pi$  nature, with more  $\pi$ -bonding, and also with significant contribution from the metal atom in the layer below the hollow. This is a complication well beyond the systematics developed by Parish [5] from a careful study of bulk compounds and will need theoretical input to obtain any quantitative answers.

It is well-known that the 5-fold symmetry which occurs in quasi-crystals gives rise to electron wave functions with quite different and unusual properties, for example leading to excellent “non-stick” behaviour for use in cookware.

It is possible that a similar situation occurs here with the 5-fold symmetry of the Marks decahedron. We propose that this is producing electron wave functions in the surface Au atoms which are conducive to creating a partial d-hole and hence the production of the magnetic moment and the conditions for ferromagnetic coupling. Proving this will take considerable sophisticated calculations. However, there is other evidence in its favour. First, this would explain why the size is so critical such that the ferromagnetism disappears at particle sizes just above 2 nm. Above this size, the Marks decahedron and its 5-fold symmetry is no longer stable and the particle reverts to the FCC structure. Further, the calculations of Doye and Wales [7] have shown that the energy minimum for the 75-atom Marks decahedron is considerably deeper for Ag than for Au, suggesting that the structure may remain stable to greater sizes for Ag. This is consistent with the larger size (4 shells) which we found for ferromagnetism in Ag, compared to 3 shells for Au [3]. This structure stability argument also explains some of the great variation observed in the measured magnetic moments per Au atom from different groups, because there is often considerable difference in the size histograms and nanoparticles which have grown beyond the Marks decahedron critical radius will not contribute any moment to the total magnetization.

We note this would make the mechanism of formation of the magnetic moments in Au nanoparticles completely different from that observed in ferromagnetic Au films [11]. In this

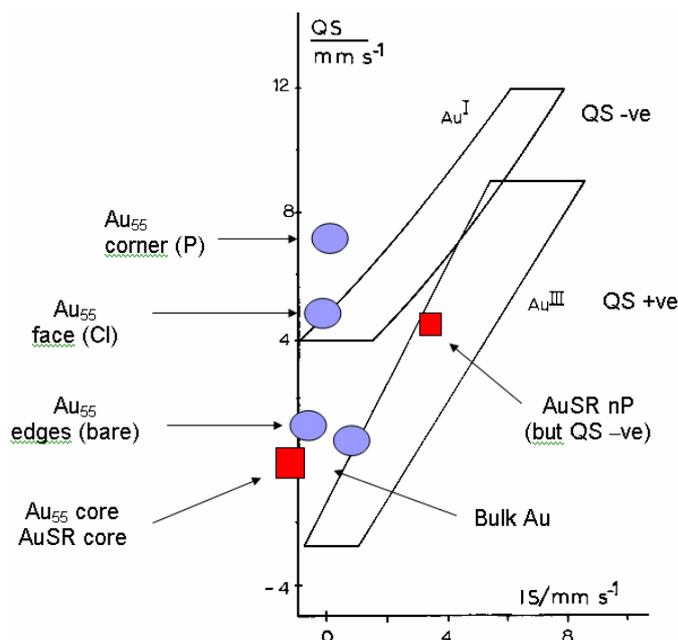


Fig. 2. Diagram of the usual Au(I) and Au(III) allowed configurations on a QS ~ IS diagram. The parameters for the capped Au<sub>55</sub> and Au nanoparticles are shown.

case, islands of insulating thiol-capped Au are formed and the Au conduction electrons describe giant orbits which can be up to  $\mu\text{m}$  size, hence generating a giant orbital contribution. Although it is stated [11] that the estimated values of the magnetic moments are in good agreement with experimental observations in thiol capped Au films and nanoparticles, we believe that the latter is fortuitous. There are other reasons for suggesting that a large orbital contribution is not present in these nanoparticles. For example, for a magnetic system with a large orbital moment, rotation under an applied field should give a remanence/saturation ratio  $\sim 0.5$ . In contrast, we get the ratio to be 0.1, with very rapid saturation, suggesting that the orbital contribution is small.

## 5. Conclusion

We have used the  $^{197}\text{Au}$  Mössbauer parameters to draw conclusions about the bonding in thiol-capped Au nanoparticles and the fraction of 5d electron hole. In particular, we have proposed that the ferromagnetic interactions in Au nanoparticles only occur when it is in the size range where the Marks decahedron is stable and that the ferromagnetism vanishes as soon as the particles assume the FCC structure of the bulk.

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