

Two dimensional electron gas confined over a spherical surface: Magnetic moment

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Abstract. Magnetism of capped nanoparticles, NPs, of non-magnetic substances as Au and ZnO is briefly reviewed. The source of the magnetization is discussed on the light of recent X-ray magnetic circular dichroism experiments. As magnetic dichroism analysis has pointed out impurity atoms bonded to the surface act as donor or acceptor of electrons that occupy the surface states. It is proposed that mesoscopic collective orbital magnetic moments induced at the surface states can account for the experimental magnetism characteristic of these nanoparticles. The total magnetic moment of the surface originated at the unfilled Fermi level can reach values as large as 10^2 or 10^3 Bohr magnetons.

1. Introduction: Magnetic properties of Au and ZnO capped NPs

In this article the characteristics of the magnetism observed in capped Au and ZnO nanoparticles is briefly reviewed. It is now well known from EXAFS analysis [1] that this anomalous magnetism is originated by the modifications of the electronic structure of the surface introduced by the capping molecules. X-ray magnetic circular dichroism, XMCD, studies have pointed out the magnetic moment determined by magnetometry actually lies in the atoms forming the NPs and is not only originated by small amounts of impurities, as the magnitude of the magnetic moment could suggest. The most important characteristics of the observed magnetic behaviour can be summarised as follows: i) in all cases the saturation magnetization that is very low, typically in the range of 10^{-1} or 10^{-2} Bohr magnetons per atom, is reached at moderate applied fields (0.5T) and ii) the magnetization values are weakly dependent of temperature in the range from 4K up to room temperature.

In some cases the magnetization curve presents hysteresis, even though generally with moderate or low coercive field and remanence. Therefore the two main question to solve were: i) the source of the magnetic moment and ii) the origin of the hysteresis, i. e. the origin of possible exchange and anisotropy.

It was found that an alteration of the electronic structure of Au NPs induced by capping with organic molecules also leads to the appearance of room temperature ferromagnetism [1]. Au NPs of 1.6 nm radius were linked to organic molecules via thiol bonds. The NPs assembly exhibited magnetization loop and ferromagnetism like response at room temperature. Even though the magnetic moment per atom is very low, typically in the range between 0.1 to 0.02 Bohr magnetons, and, therefore, is of the order of possible ferromagnetic impurities [2], subsequent X-ray magnetic circular dichroism, appropriately tuned to Au atoms [3,4], as well as Au Mössbauer spectroscopy indicated that the Au atom posses a magnetic moment [4]. Since the first XANES and EXAFS studies it was assumed that the source of the magnetism had to be linked to electrons or holes introduced by the thiol or phosphine ligands between the surface atoms of the NPs and those located at the end of the organic chain. The magnetic moment was thought of as due to uncompensated angular moment or spins of those electrons or holes introduced by the ligands. However, the observed saturation reached at room

temperature at relative low fields (1T) and the shape of the magnetization curve represented a great challenge. Even though the existence of a permanent magnetic moment were assumed, the NPs size was small enough to expect a superparamagnetic behaviour unless the magnetic anisotropy were extremely large.

Based on the magnetic behaviour of capped Au NPs we thought that capped semiconductor oxide NPs could exhibit a similar behaviour. Then the magnetic response of capped ZnO NPs was studied. The importance of the subjects is outlined below

Most of technological devices are based on the properties of semiconductors and magnetic materials. Materials able to join in a single one high velocity of processing information, as semiconductors, and information storage, as ferromagnets, should be desirable. Since the proposal by Ohno [5], extensive research work on dilute magnetic semiconductors materials have led to discover traits of ferromagnetism for semiconductors oxide compounds with and without magnetic impurities [6-14]. Despite some initial promising results in Mn:ZnO¹⁰ it is not clear if diluted magnetic semiconductors can show this high temperature ferromagnetism. Hysteresis loops have been also observed in oxide nanoparticles capped with different type of molecules [9,11]. In particular, Kittilstved et al [9] have shown that Mn:ZnO nanoparticles and thin films only exhibit room temperature ferromagnetism when capped with molecules that introduce p-type defects, whereas other capping that introduce n-type defects leads to no room temperature ferromagnetism. On the contrary for Co:ZnO films the n-type defects favour the appearance of ferromagnetism. Several class of defects as O vacancy, cationic vacancy, adatoms or doping have been invoked and speculatively suggested as sources of local magnetic moments, even in the absence of magnetic ions [7,11]. These magnetic moments would be expected to contribute to macroscopic paramagnetism. However, in many cases the samples exhibit low coercivity and low remanence hysteresis loop that seems to be weakly dependent on temperature. Since, the exchange coupling among these local moments has not been satisfactory explained [12-14] the question deals with the possible origin of such traits of ferromagnetic behaviour.

Recently some relevant experiments and calculations were carried out on ZnO, nanoparticles, NPs, [11,15] capped with different molecules. M. A. García et al [11] have shown that 10nm sized ZnO NPs, without doping with magnetic impurities, can exhibit room temperature ferromagnetism when capped with three different organic molecules, amine, thiol and topo. It was also observed that even though no differences in the structure, as determined by X-ray diffraction and transmission electron microscopy, were detected among the three type of nanoparticles, the magnetization correlated with the differences of the electronic configuration of the surface as measured by XANES. This result pointed out that traits of ferromagnetism can be observed in semiconductors NPs and perhaps films and surfaces without introducing magnetic *d* transition atoms as impurities.

Later circular magnetic dichroism experiments were performed by Chaboy et al [15] on thiol capped ZnO NPs. The results clearly indicated that the valence band formed by the Zn-3d and the O-2p overlapping bands is filled and consequently magnetically depolarised. However, the conduction band, mainly formed by empty 4sp Zn surface states, exhibits a clear magnetically polarised signal that enables to conclude that the observed magnetism is originated by 4sp electrons associated with the bonding of the capping molecules to the NP surface atoms. It is interesting to remark that polarization in Au capped NPs was observed in the 5d level but the metallic character of Au and the overlapping between bands does not allow a so clear observation as that obtained in semiconductors. First principle calculations performed by Botello-Méndez et al [16] for passivated nano-ribbons and clusters of ZnO also concluded that bonding to sulphur atoms induces a magnetic moment that could be responsible of the observed ferromagnetic responses.

In order to ascertain the modifications introduced on the surface electronic structure by capping molecules, it is worth to remark that the bonding of the carbon oxide, CO, molecule to the surface zinc ions in ZnO was studied in detail by Anderson and Nichols in 1986. They found that the effect of the complex bonding, that involves the decay to an empty low energy level of the electron that would occupy the anti-bonding state, can be summarised as the donation of one electron from the molecule to the 4sp surface orbitals of Zn [17] that are initially empty. Therefore, the polarisation of the 4sp

electrons observed by XMCD should be that of the electrons donated by the capping molecule (or surface defects in general) which are confined in a thin depth at the surface. Hence, the origin of magnetization in capped ZnO NPs must be closely related to those electrons donated by the atoms of the organic molecule that are bound to the Zn atoms of the NP surface. Consequently the relevant issue to address should be the calculation of the magnetic moment of a two dimensional electron gas confined in a spherical surface.

We outline the idea proposed by Hernando and García [18] to explain the origin of the magnetic moment in capped ZnO NPs. First the energy spectrum of the electrons confined on a spherical surface is discussed. It will be shown that for an assembly of NPs, fluctuations of NPs size as well as fluctuations in the coverage factor induce fluctuations in both Fermi level and its occupation number. For partially occupied Fermi level a permanent magnetic moment develops similarly to that induced at incomplete atomic orbitals. However, for the case of NPs the strength of the magnetic moment may be two or three order of magnitude larger than for atoms. After analysing the relative strength of the different energy terms the magnetic moment of the partially filled 4sp band of surface states is estimated [18]. Subsequently, the cause of ferromagnetic traits is discussed by taking into account geometrical deviations from the spherical symmetry. Notice that the results can be extended to any type of NPs with its band of surface states partially occupied by either electrons or holes. Finally the results predict a magnetic moment behaviour that is compared with the more important experimental characteristics of the hysteresis loop observed in capped oxide NPs.

Even though the basic idea of our proposal [18] here outlined was focused to account for the magnetism of capped oxide NPs it might be probably also valid for Au NPs. The clear separation and lack of overlapping of *d* and *sp* bands due to the semiconductor character of ZnO enables the observation of a well defined XMCD polarisation in the *sp* band¹⁵. However, XMCD polarisation observed in Au has been restricted to the accessible *d*band [3,4] that overlaps with the *p* one.

2. Energy spectrum of an electron gas confined on spherical surface.

In order to estimate the permanent magnetic moment of the electrons occupying the 4sp surface states we must begin by calculating its energy spectrum and eigenstates. Let us initially consider that the electrons donated by the capping organic molecules are confined by a Dirac δ potential to jump between surface atomic sites thus forming an electron gas depicted by its effective mass. The corresponding eigenstates of a non interacting gas confined in the spherical surface of NPs [19-23] are the spherical harmonics $Y_{l,m}(\theta,\phi)$ and their associated kinetics energy eigenvalues depend on the angular quantum number *l* as

$$e_l = \frac{l(l+1)\hbar^2}{2mr^2} = \frac{l(l+1)}{2}e_1 \quad (1)$$

where *r* is the radius of the NPs and *m* is the effective mass of the electron, that can be written as

$$m = \frac{\hbar^2}{2a^2b},$$

b being the hopping amplitude proportional to the surface band width and *a* the average

inter-atomic distance at the surface. The experimentally measured width of surface bands varies

between 0.5 and 1.0 eV [24]. Notice that e_l can be expressed as $e_l = \frac{\hbar^2}{2mr^2} = b\left(\frac{a}{r}\right)^2$ The distance, *d_l*,

between adjacent levels with quantum numbers *l* and *l+1* is given by

$$d_l = (l+1)e_l = (l+1)b\left(\frac{a}{r}\right)^2 \quad (2)$$

Consider the surface to be formed by N atoms and that there are $N_b (< N)$ electrons, denoted by $N_b = \alpha N$ capping molecules (or defects) with $\alpha < 1$, where N is of the order of $4\pi\left(\frac{r}{a}\right)^2$. If we proceed as in the case of free electrons by filling successively the levels of increasing energy given by (1) up to reach N_b and after taking into account that the maximum number of electrons that can occupy any level is given by $2(2l+1)$ it can be seen that the Fermi level is implicitly defined through the following relationship

$$N_b = \alpha 4\pi\left(\frac{r}{a}\right)^2 = 2(l_F + 1)^2 \quad (3)$$

In general l_F as defined by (3) is not an integer but the following relation can always be written

$$l_F = \sqrt{\frac{N_b}{2}} - 1 = q + x, \quad (4)$$

where q is an integer and $0 < x < 1$. The Fermi level, is then given by: $l_F = q + 1$, and must be only partially filled. According to (3), the number of electrons occupying the first q levels that are completely filled is $2(q+1)^2$. Therefore, the number, n^* , of electrons occupying the Fermi level should be $n^* = N_b - 2(q+1)^2$, that according to (4) becomes

$$n^* = 2x(2q+2+x) = 2x(2l_F+x) \quad (5)$$

Notice that the band would be filled for $\alpha=2$. As any bonding molecule contributes with an electron to the surface band the maximum possible number of electrons that is reached for a coverage factor $\alpha=1$ would correspond to a half filled band. Consequently, after capping, the surface band is generally populated less than one half of its capacity. If we restrict our analysis for NPs ranging in diameter between 1 to 20 nm, (r/a) roughly varies between 5 and 100 that correspond to N comprised in the interval 300 to 30000, respectively. Therefore, for the maximum capping coverage ($\alpha=1$), l_F would be comprised between 12 and 123.

3. Intra-band exchange interaction and spin-orbit coupling

Besides the kinetic energy the surface electrons are subjected to electron-electron interactions as well as to surface spin-orbit coupling. The relative strength of these Hamiltonian terms would determine, as it happens in atomic physics, the order of perturbation steps to approximate the wave function. In other words, the spontaneous magnetic moment of the N_b electrons of a single NP is expected to be that associated with the n^* electrons occupying its partially filled degenerated Fermi level. However, even if n^* is known the estimation of the moment requires also to know the way in which these individual moments are coupled to create the collective moment of the surface state.

When the kinetic energy is assumed to be the main contributing term to the total Hamiltonian the spherical harmonics form the complete set of eigenfunctions in which the perturbation process should be carried out. However, two limit cases of angular momentum coupling should be considered as is well known from atomic physics. For the case of electron-electron interaction larger than the spin-orbit coupling, the angular moments couple to each other according to the $L-S$ coupling. Under opposite conditions the coupling becomes $j-j$ type. Independently of the type of coupling the values of the total angular momentum quantum number, J , is the same in both cases even though the corresponding energies can differ in absolute value. As we are here only concerned with the magnetic moment the calculation will be restricted to the case of $L-S$ coupling. For the $L-S$ coupling the progressive filling of the Fermi level proceeds according to the Hund rules, i. e. maximum S and maximum allowed L . But is important to take into consideration that the estimation of the magnetic moments, obtained from the estimation of the possible J values at the Fermi level, is independent of

whether the exchange is larger or smaller than the spin-orbit coupling, provided that the distance between adjacent kinetic energy levels is larger than the spin-orbit coupling.

The importance of the spin-orbit coupling at surfaces (Rashba effect), $\gamma\sigma$, where γ is the Rashba coefficient σ the Pauli matrices, has been experimentally pointed out by many authors that measured and calculated its splitting [24-30].

4. Calculation of the permanent magnetic moment associated with the Fermi Level

As previously stated we can calculate the possible values of J in the Fermi level, characterised by l_F and occupied by $n^* < 2(2l_F + 1)$ by using either L - S or j - j coupling. Let us consider L - S or Russel-Saunders coupling. Then according to the Hund rules the electrons occupy successively the Fermi level by reaching the maximum spin and the maximum orbital momentum compatible with the maximum spin condition. The values of L and S are symmetric respect to $n^* = (2l_F + 1)$. Therefore, the following relationship holds for L and S , $L(n^*) = L(2(2l_F + 1) - n^*)$; n^* can then be restricted for calculation to the condition $0 < n^* < (2l_F + 1)$.

Then for L - S coupling, if the spectral term with lower energy is that with quantum numbers $L(n^*)$ and $S(n^*)$ the value of $J(n^*)$ corresponding the ground state is either $J = L + S$ or $J = L - S$ for negative or positive sign of spin-orbit coupling, respectively. According to the Hund rules the spectral term obtained by considering n^* electrons in the l_F level is that given by $L = \left(l_F - \frac{n^* - 1}{2} \right) n^*$. Therefore, for negative spin-orbit coupling the value of $J(n^*)$ becomes

$$J(l_F, n^*) = \left(l_F + 1 - \left(\frac{n^*}{2} \right) \right) n^* \quad (6)$$

whereas for positive spin-orbit coupling, $J(l_F, n^*)$ can be written as

$$J(l_F, n^*) = \left(l_F - \left(\frac{n^*}{2} \right) \right) n^* \quad (7)$$

In general the spin-orbit coupling is negative for orbital level occupied below one half of the total occupation and positive for higher occupation numbers.

Figure 1 illustrates the J dependence on n^* for the typical size of NPs reported in the literature and for negative sign of spin-orbit coupling. It can be seen that the values of $J(l_F, n^*)$ for $l_F = 8, 20, 40$ and 80 are very large when compared to the usual strength of the atomic angular moments.

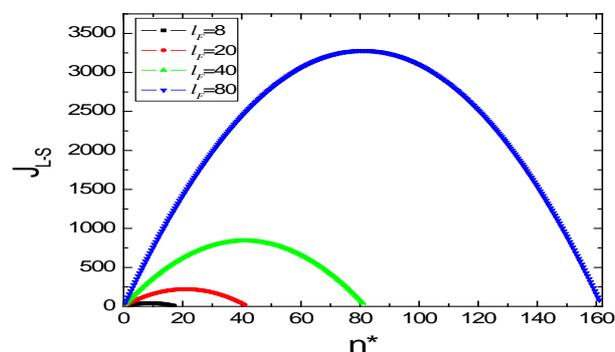


Figure 1. J values as a function of n^* obtained according to (4) for l_F ranking between 8 y 90, that are the expected values for normal NPs sizes as indicated at page 4. The average values $\langle J \rangle$ obtained for uniform n^* distribution and obtained from (7) are, 21, 133, 533 and 2133 for $l_F = 8, 20, 40$ and 80 respectively.

5. The permanent magnetic moment of an assembly of NPs.

In a NPs assembly both $\frac{r}{a}$ and α shall present fluctuations respect its average values $\left\langle \frac{r}{a} \right\rangle$ and $\langle \alpha \rangle$ that will give rise, according to (3), to I_F and n^* fluctuations. In fact the following approximately relationship is easily derived from (3)

$$\frac{\Delta I_F}{\langle I_f \rangle} \approx \frac{\Delta r}{\langle r \rangle} + \frac{\Delta \alpha}{\langle \alpha \rangle} \quad (8)$$

Notice that, for $\langle I_f \rangle = 100$, the relative fluctuation in radius that leads to a change of Fermi level, $\Delta I_F = 1$, is given by 0.01. Therefore small fluctuations respect to the experimental ones must give rise to a wide spectrum of Fermi levels with occupation, n^* , ranging continuously between 1 and $2(2I_F + 1)$. For a constant I_F and a uniform distribution of n^* the average value of the quantum magnetic moment number, also indicated in Figure 1 caption, becomes:

$$\langle \mu \rangle_{I_F} = \mu_B \langle g_J J(I_F, n^*) \rangle \quad (9)$$

where g_J is the Landé factor for the particular $2J+1$ subspace corresponding to the quantum number J , i. e. $g_J = 1 + \frac{j(j+1) - L(L+1) + S(S+1)}{2J(J+1)}$.

The order of magnitude of the average $\langle \mu \rangle_{I_F}$ when n^* varies between 1 and $2(2I_F + 1)$ can be estimated from the analytical expressions (6) or (7), after approximating³² $g_J = 1$. For n^* larger than $2(2I_F + 1)$, negative spin-orbit coupling, (6) yields

$$\langle \mu \rangle_{I_F} = \frac{1}{3} (I_F^2 + 2I_F + 1) \mu_B \quad (10)$$

whereas, for n^* smaller than $2(2I_F + 1)$, positive spin-orbit coupling, (7) yields

$$\langle \mu \rangle_{I_F} = \frac{1}{3} (I_F^2 - \frac{1}{2}I_F + \frac{1}{2}) \mu_B \quad (11)$$

$\langle \mu \rangle_{I_F}$ expressed by (10) and (11) is the average magnetic moment of the NPs assembly for a constant I_F and a uniform n^* distribution and is given by

$$\langle \mu \rangle_{I_F} = \frac{1}{3} (I_F^2 + \frac{1}{4}I_F + \frac{1}{4}) \mu_B \quad (12)$$

From (10) and (11) it becomes evident that for large I_F , i. e. $I_F > 10$, the order of magnitude of the average magnetic moment at I_F is given by $\mu_B I_F^2$.

It is remarkable to observe that the nanometric scale reflected in the ratio $\frac{a}{r}$ governs, i) the importance of the kinetic energy as it enhances d_j in (2) and ii) the value of the average magnetic moment per atom that being originated exclusively at the surface of the NPs becomes macroscopically negligible when the ratio $\frac{a}{r}$ becomes of the order of the sensitivity and precision degree of the magnetometry instrument.

6. Effect of the applied magnetic field

When a magnetic field is applied along the polar or z axis of the NPs the spherical symmetry of the Hamiltonian is partially broken by the field. As thoroughly analysed by Huang and Gumbs [23], in the low field range the spectrum of the kinetic energy only is modified by a perturbation that splits the degenerated ground state in its $2J+1$ components and induces a diamagnetic moment given by

$N_b \frac{e^2 B r^2}{4m}$ that, even though is much larger than that observed for atoms as a consequence of the mesoscopic scale of the orbits³³, it remains almost negligible for $J \neq 0$, since, for $B=1\text{T}$, it is of the order of $10^{-3} \mu_B N_b$ (low field approximation in refs [22] and [23]). It is to be remarked that enhancement of the orbital moment at plane surfaces, associated with the surface broken symmetry, has been observed and reported by different authors [34,37].

According to our calculations the NPs should exhibit giant paramagnetism; reaching saturation under moderated fields even at room temperature. Notice that with a surface collective magnetic moments of the order of $g \mu_B I_F^2$, (8), an applied magnetic field of 1T would induce a maximum Zeeman splitting of $2 \mu_B I_F^2$ that is larger than the thermal energy at room temperature for any $I_F > 10$. It can be concluded that the Langevin or Brillouin curve depicting the paramagnetism of the NPs is

close to saturation, i.e. , $\frac{\mu_B \left(\frac{1}{3} I_F^2 \right) B}{kT} \geq 1$, for $B=1.5\text{T}$ and $T=300\text{K}$ if I_F is larger than 10, that is a very reasonable value for the size of the NPs experimentally studied, and coverage factor of the order of 0.5. The experimental saturating field is around 1.5 T .

7. Conclusions

In conclusion it has been shown that NPs with radius below 10 nm, even being of diamagnetic substances, can exhibit giant paramagnetism when capped with molecules that act as donors or acceptor of surface electrons. The experimental values are very well reproduced in the framework we have reported here. The magnetic saturation, typically of 0.1 to 0.01 Bohr magneton per NPs atom, is reached under moderated fields at room temperature, in the range between 1 and 2 T, due to the large strength of the collective magnetic moment of the NP, generally larger than 100 Bohr magnetons . The source of the magnetic moments is the two dimensional electron (or hole) gas introduced by impurities, as for instance capping molecules, that occupy previously empty surface states (or introduce holes in a filled band). Orbital and spin angular moments are formed at the generally unfilled Fermi level of the system that is confined on a spherical surface. The unfilled Fermi level of the surface band is characterised by a collective magnetic moment just like an atomic orbital but with much larger quantum number.

The effect of confinement at the NPs surfaces of the electrons actives in the bonds to the capping molecules together with the unfilled character of its Fermi level are found to be the source of the exotic magnetism of these non-magnetic in bulk, NPs.

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