

# Magnetic Circular Dichroism and the Nature of Ferromagnetism in Colloidal Gold Nanoparticles

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The spectra of optical absorption and of magnetic circular dichroism (MCD) have been measured in the 350–1150 nm wavelength range for a set of colloidal solutions containing Au nanoparticles with the average size of 6 nm having thiolate coatings with different degrees of chirality. The form of absorption and MCD spectra suggests the dipole character of interband transitions involving the  $5d-6(sp)$  orbitals. The absence (within the experimental error) of the dependence of the MCD spectra on the coating type rules out the hypothesis on the orbital nature of the observed magnetism. We argue that the spin polarization plays the dominant role in the magnetism of gold nanoparticles with a thiolate coating.

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Metal nanoparticles attract significant interest of physicists, chemists, and engineers since they are promising for high-density data storage [1], catalysis [2], sensors [3], targeted drug delivery [4], and a new generation of electronic devices (such as single-electron transistors [5]). They are also important for fundamental physics [6]. The unique properties of metal nanoparticles are directly related to their size. They are in drastic contrast to the corresponding characteristics of bulk materials [7, 8]. In addition to the accurate control of size and shape of nanoparticles, there appears such an important problem as their stability. For obtaining the specified nanoparticle sizes, stabilizers of different kinds are used, for example, surfactants [9], polymers [10], and thiol-functionalized molecules [11]. Thiol-stabilized gold nanoparticles have been studied better than the other ones. The structure of their thiolate monolayers has been revealed by different methods. Their stability stems from the strong Au–S bond providing their high stability in solutions even at elevated temperatures. This makes them convenient objects in the studies involving nanoparticles. The observation of their magnetic properties (see, e.g., review [12]), natural circular dichroism (see, e.g., [13]), and magnetic circular dichroism (MCD) [14, 15] in colloidal solutions of gold nanoparticles coated with different stabilizing molecules has attracted additional attention to the

properties of nanoparticles [12]. It became clear that the circular dichroism appreciably depends on the chirality of the coating covering nanoparticles. In bulk gold, the magnetism does not manifest itself, and the  $5d$  bands are completely occupied and located at 2.4 eV below the Fermi level [16]. Therefore, a model based on the orbital magnetism has been put forward for explaining the behavior of gold nanoparticles [17]. To check the hypothesis on the orbital nature of the magnetism in gold nanoparticles, we produced and studied a set of nanoparticle samples differing in the chirality of the thiolate coating. It is well known that the MCD is proportional to the total magnetic moment, including the spin and orbital components. Similar to the situation with a spherically symmetric atom, which can be in the state with nonzero orbital angular momentum, a spherically symmetric nanoparticle can also have a nonzero orbital angular momentum. The molecules of the stabilizer, in turn, can also have their own orbital angular momenta, which obviously depend on the degree of their chirality. Owing to the coupling between a nanoparticle and molecules of the stabilizer, the total orbital angular momentum should also depend on the degree of chirality. Therefore, observation of the dependence of the MCD signal on the degree of chirality could verify the hypothesis on a significant contribution related to the orbital magnetism. On the contrary, the MCD sig-

nal independent of the degree of chirality of the stabilizer molecules would suggest a small contribution coming from the orbital angular momentum and the dominant role of the spin magnetism. Below, we describe the results of the measurements of the absorption and MCD spectra. We discuss a mechanism underlying the excitation of the surface plasmon resonance in gold nanoparticles and the formation of MCD related to the dipolar  $5d-6(sp)$  interband transitions, and also the role of the hybridization between the electronic states of gold and sulfur entering into the composition of the thiolate coating. The independence of MCD from the degree of chirality allows us to argue that the magnetism here has the spin nature. This conclusion agrees well with the direct experimental determination of the small orbital contribution (in comparison to the spin one) to the X-ray magnetic circular dichroism of gold nanoparticles with other molecular stabilizers (see below the discussion of [18]).

Gold nanoparticles with thiolate (chiral or achiral) monolayer coatings were prepared according to a technique slightly modified in comparison to that described in detail in [13]. First of all, we produced gold nanoparticles 6 nm in size with a labile dodecylamine coating using the Peng technique [19]. Then, dodecylamine molecules in the monolayer were replaced by thiolate fragments by the reaction of exchange with the corresponding  $\alpha,\omega$ -thiocarbon acids, which were then deprotonated by tetramethylammonium hydroxide for obtaining water-soluble nanoparticles. We used either achiral 11-mercaptoundecanoic acid (MUA) or chiral  $\alpha,\omega$ -thiocarbon acids ( $\text{HS}(\text{CH}_2)_{10}\text{CONH-CH(R)COOH}$ , MUA-L-AA) prepared by combining MUA with L-amino acids according to the technique reported in [20]. We obtained chiral nanoparticles with three amino-acid residuals, L-alanine ( $\text{R} = \text{Me}$ ), L-serine ( $\text{R} = \text{CH}_2\text{OH}$ ), and L-phenylalanine ( $\text{R} = \text{CH}_2\text{Ph}$ ), which further on are referred to as Au-L-Ala, Au-L-Ser, and Au-L-Phe, respectively. In our work, we studied gold nanoparticles with the average size of 6 nm (with the standard deviation  $\sigma = 9\%$ , according to the results of the small-angle X-ray scattering (SAXS) obtained at the Kurchatov Centre of Synchrotron Radiation and Nanotechnologies). This implies that the average composition of nanoparticles is  $\text{Au}_{6670}\text{S}_{530}$ , where S is chiral or achiral thiolate. Thus, the volume density of the thiolate groups in the solution (at the surface of nanoparticles) was a factor of 12.6 lower than the density of gold atoms. A schematic image of the particles is presented in Fig. 1. We studied the solutions with the following densities of gold nanoparticles:

- (i) AuMUA (nanoparticles with the achiral monolayer), 19.2 mmol/L;
- (ii) Au-L-Ala (chiral nanoparticles), 2.63 mmol/L;
- (iii) Au-L-Ser (chiral nanoparticles), 2.39 mmol/L;
- (iv) Au-L-Phe (chiral nanoparticles), 20.2 mmol/L.

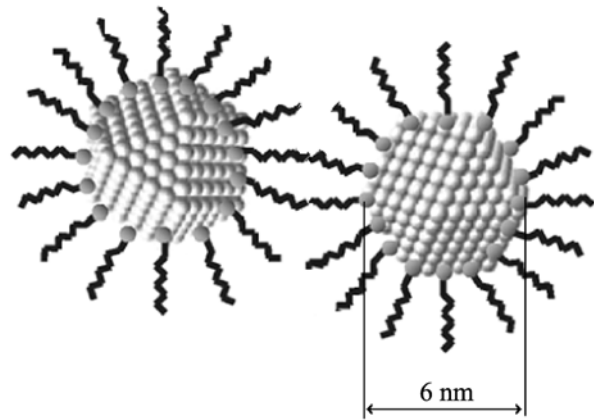
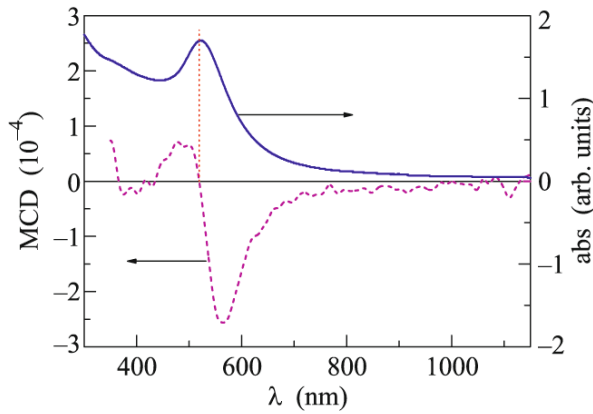


Fig. 1. Schematic image of gold nanoparticles stabilized by the monolayer thiolate coating.

The magnetic circular dichroism was measured in the 350–1150 nm wavelength range using the original spectropolarimeter setup designed at the Kirensky Institute of Physics based on the MDR-2 monochromator. We used the modulated polarization of the light wave from right to left circular polarization. The modulator is a prism made of fused quartz with an attached piezoceramic element. An ac electric signal with the frequency  $\omega$  corresponding to the eigenfrequency of the system applied across the piezoceramic element leads to the excitation in quartz of a standing elastic wave. In the absence of acoustic excitation, the prism is optically isotropic. When the compression half-wave passes through the prism, the propagation direction of the acoustic excitation (along the horizontal axis of the prism) becomes the “slow” axis of the prism. When the second half-wave passes through it (stretching half-wave), the situation is the opposite: the stretching axis becomes the “fast” axis of the prism. If the prism is exposed to linearly polarized light with the polarization plane rotated by an angle of  $45^\circ$  about the horizontal axis of the prism, then, in the case of excitation of the standing acoustic wave in it, the output light will have either right or left circular polarization alternating with the frequency of the acoustic vibrations of the prism. If the sample under study exhibits the effect of MCD, the absorption coefficients for the right- and left-polarized (with respect to the direction of the sample magnetization) light waves are different. Owing to this, the luminous flux passed through the sample and incident on the photomultiplier has a modulated intensity. The dc component of the photocurrent was maintained at the same level when the wavelength varied. As a result, the output ac signal of the photomultiplier was proportional to the magnitude of MCD. The magnetic circular dichroism was measured as the difference of two signals corresponding to two opposite directions of the applied magnetic field. The calibration of the MCD absolute value was per-



**Fig. 2.** Absorption and MCD spectra for the colloidal aqueous solution of gold nanoparticles with the chiral coating.

formed according to the technique described in [21]. The MCD measurements were performed at the applied magnetic field equal to 0.5 T at room temperature. The sensitivity of the MCD measurements was  $10^{-5}$  and the spectral resolution was  $20 \text{ cm}^{-1}$ . The optical absorption spectra were recorded with the use of a Shimadzu UV-3600 spectrometer.

Figure 2 shows the absorption and MCD spectra for colloidal gold nanoparticles dispersed in an aqueous solution (Au-L-Ala sample) recorded at room temperature. The peak in the absorption band is observed at a wavelength of 523 nm. At the same wavelength, the MCD changes its sign. We can see that the S-shaped MCD curve is not symmetric: the amplitude of the negative peak by about a factor of 3 exceeds the amplitude of the positive peak. The picture is similar for all other samples. The values of absorption and MCD normalized with respect to the nanoparticle density are nearly independent of the degree of chirality of the coating (Fig. 3). The peak in the absorption is in agreement with the results reported in [22–24], where it is attributed to the surface plasmons. In the general case, the MCD is described by the expression

$$\Delta k(\omega) = -\frac{4\pi}{hc} N_a \left\{ \frac{4\omega_{ja}\omega^3(\omega_{ja}^2 - \omega^2)\Gamma_{ja}}{h[(\omega_{ja}^2 - \omega^2) + \omega^2\Gamma_{ja}^2]^2} A + \frac{\omega^3\Gamma_{ja}}{(\omega_{ja}^2 - \omega^2)^2 + \omega^2\Gamma_{ja}^2} \left[ B + \frac{C}{kT} \right] \right\} H_z, \quad (1)$$

where  $N_a$  is the number of molecules in the  $a$  state per unit volume,  $\Gamma_{ja}$  approximately coincides with the half-width of the spectral line,  $\omega$  is the current frequency, and  $\omega_{ja}$  is the frequency of the optical transition. Usually the MCD includes three contributions,  $A$ ,  $B$ , and  $C$  (see, e.g., [25, 26]). The diamagnetic contribution  $A$  is proportional to the magnetic-field-

**Fig. 3.** Amplitude of the negative peak in MCD versus the degree of chirality of the coating in samples: (1) AuMUA (nanoparticles with the achiral monolayer), (2) Au-L-Ala, (3) Au-L-Ser, and (4) Au-L-Phe (nanoparticles with the completely chiral monolayer).

induced splitting of the electronic states and is independent of temperature. The paramagnetic contribution  $C$  is proportional to the difference between the thermal occupation numbers for the components of the ground state split by the applied magnetic field and hence it is a function of temperature. Contribution  $B$  results from the polarization of the optical transitions in the applied magnetic field. It is described by the dispersion law the same as for the  $C$  term and is also referred to as the paramagnetic term. This term arises owing to the mixing of the states in the applied magnetic field and therefore does not depend on temperature (within a limited temperature range). The observed (see Fig. 2) relation of the MCD spectra to the surface plasmon resonance is characteristic of contribution  $A$ , which vanishes at the resonance frequency.

According to its form, the MCD spectrum corresponds to the  $A$  contribution to the MCD from change to for the electron transition from the nondegenerate ground state to the degenerate excited state. In this case, however, the bands turn out to be asymmetric: the negative part of the MCD signal is much larger than the positive one. These observations demonstrate that the MCD curve does not correspond to the pure  $A$  contribution to the MCD. The number of excited states is large and this suggests an appreciable mixing in the excited spin-orbit state. The absence (within the experimental error) of the dependence of the MCD spectra on the degree of chirality (see Fig. 3) leads us to the conclusion that the contribution of the orbital magnetism is insignificant. To find out the mechanism of the spin polarization, we need to discuss in more detail the changes in the electronic states on the surface of the nanoparticle. It is easy to estimate that the number of surface atoms in a gold particle with the total number of atoms  $N_A \sim 10^3$  reaches about 50% of

the total number [27]. This leads to an increase in the degree of localization for all electrons. However, this effect is the most clearly pronounced for  $5d$ -electrons of gold. In addition, the role of the chemical bonds of the surface metal atoms to the atoms in molecules of the coating becomes more important. The occupancy of  $d$ -states determines the intensity of the white line corresponding to the  $2p-5d$  excitations in the XANES spectra. For bulk gold, this intensity is quite low and does not vanish only owing to a weak  $s-p-d$  hybridization [28]. In nanoparticles with the thiolate coating, there appears the chemical  $Au^{d+}-S^{d-}$  bond with the partial charge transfer from gold to sulfur [29]. As a result of the hybridization between the  $sp$ -states of sulfur and the  $d$ -states of gold, the fraction of unoccupied  $d$ -states at the Fermi level increases. This is verified by the growth in intensity of the white Au  $L_{2,3}$  line in the XANES spectrum [28, 30]. Such a conclusion is also supported by the data of the X-ray photoelectron spectroscopy (XPS), which indicate the enhanced localization of  $d$  holes at gold [28]. The changes in the occupancy of the  $d$ -electronic states and their stronger localization in comparison to bulk gold lead also to modifications in the exchange interaction, providing the possibility of spin ordering in the system of  $d$ -electrons. For nanoparticles with another coating (Au-PAAHC), the spin character of magnetism has recently been confirmed by the measurements of the X-ray magnetic circular dichroism (XMCD). The corresponding ratio of the orbital and spin magnetic moments is  $\mu_L/\mu_s = 0.145$  [8].

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