

## Quantum Confinement Features in EPR and UV-vis Spectra of Al/Au Nanosystems

V.V. Kislyuk<sup>1</sup>, A.K. Melnyk<sup>2</sup>, N.I. Buryak<sup>3</sup>, V.V. Trachevskij<sup>4</sup>

<sup>1</sup> G.V. Kurdyumov Institute of Metal Physics, NASU, 36, Vernadskyi Prosp., 03142 Kyiv, Ukraine

<sup>2</sup> Institute for Sorption and Problems of Endoecology, NASU, 13, Naumov St., 03028 Kyiv, Ukraine

<sup>3</sup> V.I. Vernadskiy Institute of General and Inorganic Chemistry, NASU, 32/34, Acad. Palladin Ave., 03680 Kyiv, Ukraine

<sup>4</sup> Technological Center, NASU, 13, Pokrovska St., 04070 Kyiv, Ukraine

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The composite Al/Au nanosystems synthesized by co-reduction from solution (with tannin and sodium citrate as reducing agent) are studied by electron paramagnetic resonance (EPR) and UV-vis electron absorption spectroscopies. A fine structure revealed in line with  $g = 2.062$  (associated with particles whose paramagnetism originates from odd number of gold atoms) is attributed to the discrete electronic states of an unpaired electron in a joint electron structure of a polyatomic nanoparticle. This fine structure manifests itself as a sequence of the resonance signals with close values of their  $g$ -factors. The UV-vis absorption spectra of the Al/Au nanocomposite solution contain equidistant absorption bands with 0.73-0.7 eV energy differences between the adjacent peaks. These features are attributed to the quantum confinement effects in the Al/Au nanocomposite system. The estimates made on the basis of the experimental data outline the size of the gold containing nanoclusters which in their paramagnetic form are of several nm in diameter.

**Keywords:** EPR, UV-vis absorption, Confinement, Nanoparticles, Paramagnetism, Superatom.

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### 1. INTRODUCTION

Gold containing nanocomposite systems attract researchers not only due to their wide range of application [1-5] including biology, medicine and other important fields of human being. These materials demonstrate also new magnetic properties [6-10] absent in the constituent metals in their bulk form.

A possible origin of the paramagnetic behavior of gold-containing nanocomposites is found to be the following [9, 10]: i) presence of the  $Au^{2+}$  intermediate state of incompletely reduced and isolated gold atom; ii) radical formation at the supporting molecule or radical produced as a result of interaction between the supporting surrounding and  $Au^+$  intermediate; iii) appearance of nanoclusters with odd number of completely reduced gold atoms, i.e. in the  $Au^0$  state.

These nanoclusters are fragments of a more complex aggregate structure comprising all the above components produced via both acid-base and redox transformations.

This paper focuses on the study of the core containing gold in its zero-valence form which is surrounded by a complex shell of structuring and stabilizing role, as it follows from the NMR data [11].

The content of the shell includes aluminum containing oxide supporting structure stabilized by linkage system within the supermolecular complex of tannin-citrate-water [11]. Such a polyatomic cluster is actually a superatom [12]. This is a relatively new class of species, and experimental evidences and data about their behavior and features are of particular importance for more systematic understanding of the underlying processes.

### 2. EXPERIMENT

#### 2.1 Synthesis of Al/Au Nanocomposite Solution

Au/Al nanocomplex was synthesized by co-reduction method [7] modified according to peculiarities of the re-

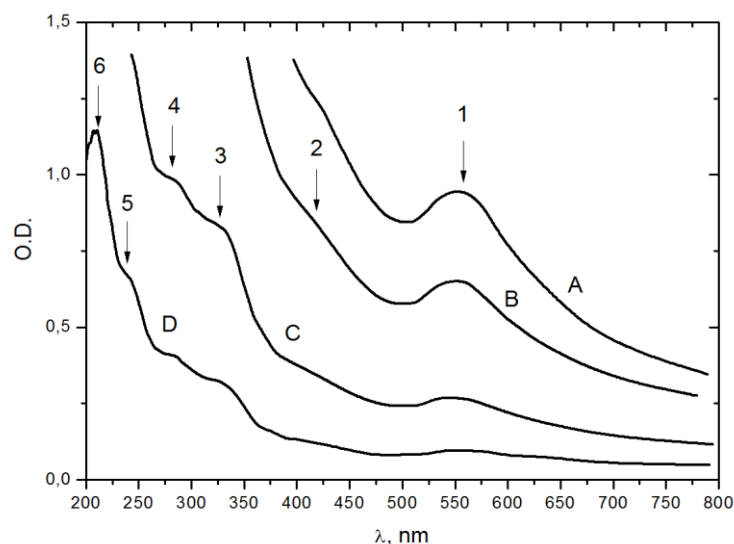
dox processes. The chlorine containing compounds of Au and Al ( $HAuCl_4$  and  $AlCl_3$ ) dissolved in water was used as a precursor ("metal containing solution"). 0.55 % solution of  $HAuCl_4$  was produced by dissolving gold (of 99.99 % purity) filings at the ambience of chlorine gas [13]. The gaseous chlorine flowed from the reactor with potassium permanganate where hydrochloric acid was added with low rate (approximately 0.01 ml per 5 min).

1 % solution of the aluminum chloride was prepared from  $Al(OH)_3$  powder with hydrochloric acid poured slowly till stoichiometric ratio and left for a day. Then water was added in the amount corresponding to 1 % concentration.

The "metal containing solution" comprised of 5.45 ml of the 0.55 % solution of the gold compound and 6 ml of the 1 % solution of the aluminum containing constituent. Finally, water was added till 240 ml volume. To study Al influence on the final paramagnetic properties, we used the precursor solution with sufficient excess of the aluminum content followed by the proportionally increased amount of the hydrochloric acid. In this case soda was used to regulate the pH value of the metal-containing solution.

The "reducing solution" contained the mixture of two water solutions: 3 ml of 1 % tannin solution and 12 ml of 1 % solution of sodium citrate; 25 mM solution of equimolar amount of sodium carbonate was added as a buffer. Then,  $H_2O$  was added in amount to reach 60 ml volume of the whole mixture.

The "metal containing" and "reducing" solutions were heated separately to 45-50 °C and mixed together under intense stirring for 10 min. Then, the final product containing the Al/Au nanosystem was left to cool down to room temperature. One sample was prepared with lack (as to the reaction stoichiometry) of the "reducing solution" to check the role of the reducing agents on the magnetic properties of the final Al/Au nanosystem.



**Fig. 1** – UV-vis absorption spectra of the Au/Al nanocomposite solution (after the complete reduction) placed in cuvettes with various thicknesses along the optical path: A – 1 cm; B, C, D – 0.5 cm. C, D – diluted solutions: C – twice, D – four times as to the initial concentration. The values of peaks are represented in Table 1

**Table 1** – Values of the wavelength  $\lambda_i$  of peaks in UV-vis spectra (Fig. 1), the corresponding energies of optical transitions  $h\nu_i$  ( $i$  is the number of a transition indicated in Fig. 1) and differences of two adjacent transitions  $h\nu_{i+1} - h\nu_i$

$i$	$\lambda_i$ , nm	$h\nu_i$ , eV	$h\nu_{i+1} - h\nu_i$ , eV
1	557	2.226	0.740
2	418	2.966	0.735
3	335	3.701	0.727
4	280	4.428	0.738
5	240	5.166	0.738
6	210	5.904	–

## 2.2 EPR

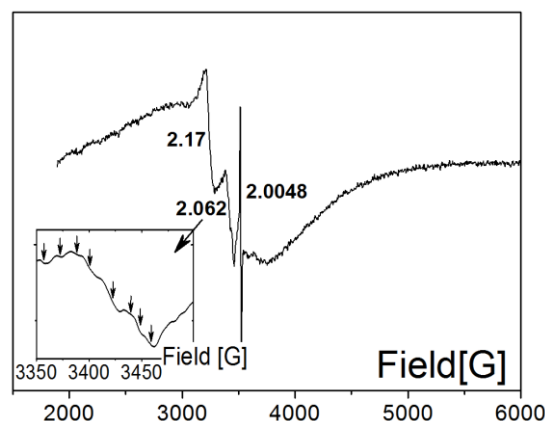
The paramagnetic properties of the formed system were studied for the solid species separated from the solution and dried at a temperature not exceeding 50 °C by different methods: i) centrifugation and separation of the solid residue; ii) salting out from the Al/Au solution with dioxane; iii) lyophilic drying of the solution with increased Al content; iv) lyophilic drying of the solution with stoichiometry shifted toward lack of the reducing constituent.

EPR spectra were recorded on a X-band spectrometer Bruker Elexsys E580 at room temperature (295 K). The EPR spectra recording conditions were as follows: frequency 9.87 GHz; microwave power 4 and 16 mW; modulation intensity 5 G with modulation frequency 100 kHz; scan width 600 mT and 51.2 mT; resolution 2048 points; conversion time 117 ms; time constant 81 ms; number of scans 4 and 16. Before spectral investigation, samples of the studied nanocomposites were placed in glass capillaries with a diameter of 1 mm and then inserted into standard 3 mm quartz ampoule (Norrell). Sample of diphenylpicrylhydrazyl (DPPH) with  $g = 2.0036$  was used for the spectrometer calibration.

## 2.3 UV-vis Absorption

UV-vis electron absorption spectra were registered at 200-800 nm range with Specord facility for solution

placed into cuvettes of 1 cm and 0.5 cm optical length. To adjust the level of the signal for the short wave length range (with strong absorption), the spectra were registered subsequently for solutions diluted twice and four times as to the initial concentration.



**Fig. 2** – EPR spectrum of the solid sample lyophilized after centrifugation from the solution of stoichiometric content. **Inset.** Detailed fragment of the central line with  $g = 2.062$

## 3. RESULTS AND DISCUSSION

The UV-vis electron absorption spectra (Fig. 1) are revealed to contain a set of discrete optical transitions with  $\delta = 0.73$ - $0.74$  eV equidistant increment (Table 1). This  $\delta$  value points to the particle size of about several nm in accordance with the theoretical predictions by Halperin, Kubo [14, 15] and other authors who analyzed quantum confinement of electron energy levels in small metal clusters.

In addition, their models describe prerequisites for emergence of magnetic properties, particularly paramagnetism due to odd number of electrons at the collective orbital within the cluster. These features are taken as argumentation to interpret i) the origin of the line with  $g \sim 2.062$  as related to odd number of electrons in the nanoparticle; ii) the fine structure revealed while

analyzing the contour of this line [10]. The model based on Kawabata's theory [16] simulated the discreteness of the electron levels in the collective electronic structure of the cluster explaining the features of the EPR line [10].

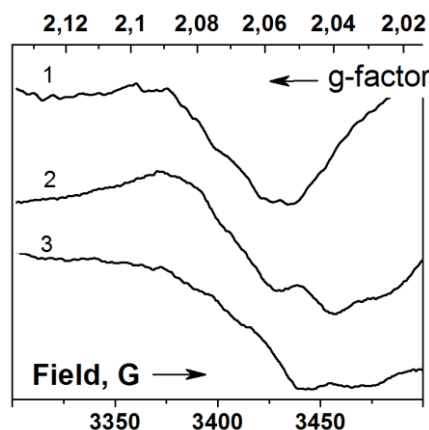
Parameters of the EPR spectrum measured in this research (Fig. 2) demonstrate some analogy with the above concept as to the nature of the paramagnetic behavior of the gold containing clusters, which is revealed in the value of  $g$ -factor (2.062) as well as the existence of the fine structure pointing to the discreteness of the levels (with approximately 12 mT spacing) in spin subsystem of the collective electron structure (Fig. 2, inset). Hence, the existing models are applicable to the system of the Al/Au nanoclusters, and the fine structure observed in the EPR line ( $g = 2.062$ ) for the systems in question reflects the discrete nature of the energy levels due to the confinement effect.

The evolution of the spectral behavior versus various factors concerning the technological routes of the sample synthesis and methods of their separation from solutions demonstrates the influence of the charge, functional state and nature of the supporting surrounding on the confinement conditions. In particular, these factors modify the boundary conditions for the models.

Fig. 3 shows the system of the quantum levels which transforms depending on the nature and ratio of the factors realized in each specific variant of the technological route for a final product. The EPR spectrum for the sample prepared by salting out with dioxane has a "blurred" peculiarities (Fig. 3, curve 1) as compared to those of the centrifuged sample (Fig. 2, inset), which is consistent with the model where boundary conditions at the cluster surface play crucial role. In this case (Fig. 3), the boundary conditions change drastically due to disappearance of the radical charge in the supporting surrounding. The radical charge is revealed as line with  $g = 2.0048$  only for the centrifuged sample (Fig. 2).

Moreover, the peculiarities observed in the spectrum for the samples prepared with deviations from the stoichiometry (Fig. 3, curves 2, 3) are, likely, attributed to clusters of various sizes and nature of the supporting molecular matrix. This assumption refers to the results

of the research [17] where  $g$ -factor drifts as a function of the size of the heteroatomic cluster with unpaired electron injected via photochemical process. The shift observed in our case toward reduced values of the  $g$ -factor corresponds to the cluster enlargement as it follows from the established reverse relationship between  $g$ -factor value and a nanocluster size [17].



**Fig. 3** – EPR spectra of the samples prepared by different techniques: 1 – salting out with dioxane and drying; 2 – lyophilic drying of the solution with Al excess; 3 – lyophilic drying of the solution with lack of reducing agent

#### 4. CONCLUSIONS

The discreteness of the electronic structure is observed for the clusters with odd number of gold atoms, which is revealed both in the UV-vis electron absorption spectra (with equidistant distribution of the transitions with 0.73-0.74 eV spacing) and in the EPR spectra (with increment 0.12 mT). The model is stated on the basis of the actual understanding of the energetic structure in the clusters of the size and content in question. Particularly, the discreteness characteristics observed for the nanoparticles stabilized in the matrix of various nature corresponds to the particle size of approximately several nanometers.

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**Ознаки квантово-розмірного квантування в спектрах ЕПР та UV-vis наносистем Al/Au**В.В. Кислюк<sup>1</sup>, А.К. Мельник<sup>2</sup>, Н.І. Буряк<sup>3</sup>, В.В. Трачевський<sup>4</sup><sup>1</sup> *Інститут металофізики ім. Г.В. Курдюмова, НАН України, бульвар Вернадського 36, 03142 Київ, Україна*<sup>2</sup> *Інститут сорбції та проблем ендоекології НАН України, вул. Наумова 13, 03028 Київ, Україна*<sup>3</sup> *Інститут загальної та неорганічної хімії ім. В.І. Вернадського НАН України, просп. Академіка Палладіна 32/34, 03680 Київ, Україна*<sup>4</sup> *Технологічний центр НАН України, вул. Покровська 13, 04070 Київ, Україна*

Композитна наносистема Al/Au, синтезована методом співвідновлення з розчину (з використанням таніну та цитрату натрію як відновників), вивчалась методами ЕПР-спектроскопії та спектроскопії електронного поглинання світла в УФ та видимому діапазонах. Виявлену тонку структуру лінії з  $g = 2.062$  (пов'язаної з наночастинками, парамагнітні властивості яких викликані непарною кількістю атомів золота в нанокластері) віднесено до наявності дискретності електронних станів неспареного електрону в об'єднаній електронній оболонці багатоатомної наночастинки. Ця тонка структура проявляється як послідовність резонансних сигналів з близькими значеннями  $g$ -факторів. Електронні спектри оптичного поглинання розчину наноконкомпозиту Al/Au складались зі смуг поглинання, які слідували еквідистантно з різницею енергій фотонів, що відповідають максимумам сусідніх смуг 0.73-0.74 eV. Виявлені спектральні особливості пов'язані з квантово-розмірними ефектами в наноконкомпозитній системі Al/Au. Оцінки, зроблені на основі експериментальних даних, показують, що розмір кластерів золота, відповідальних за парамагнітні властивості, становить близько декількох нм у діаметрі.

**Ключові слова:** ЕПР, Електронне поглинання UV-vis, Квантово-розмірне квантування, Наночастинки, Парамагнетизм, Суператом.