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EPR spectra analysis of photo-magnetic properties of EuO nanocrystals

Yasuchika Hasegawa, Yuji Wada *, Shozo Yanagida **

Material and Life Science, Graduate School of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan

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Abstract

The temperature dependencies of magnetic susceptibility *c* of the europium oxide (EuO) nanocrystals were examined. The experimental Bohr magnetons (*p*) for EuO nanocrystals agreed well with the theoretical *p* for the $4f^7$ configuration (Eu(II)). A dramatic increase in magnetization of the EuO nanocrystals under UV irradiation at room temperature was observed by photo-magnetic measurements superconducting quantum interface device (SQUID with optical fiber). This increase in magnetization under UV irradiation can be explained by the occurrence of a d–f exchange interaction of conductive electrons in the 5d band (magnetic exciton). We suggest a mechanism in which the photo-magnetization increases by the presence of an exciton band in the UV region for the polyurea-modified EuO nanocrystals. In order to confirm the magnetic exciton of EuO nanocrystals, we carried out the electron paramagnetic resonance (EPR) measurements under UV irradiation, showing the formation of photo-active species in EuO nanocrystals.
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1. Introduction

Europium oxide (EuO) has attracted considerable interest because of some physical features such as optical, magnetic and electronic properties [1,2]. The theoretical quantum-confinement model predicts the enhanced luminescence and specific magnetic properties of nano-sized Eu(II) semiconductors [3,4]. Recently, we successfully prepared EuO nanocrystals (average diameter: 3.4 nm) by photochemical reduction of $Eu(NO_3)_3$ in the presence of urea and methanol as a solvent [5]. The EuO nanocrystals exhibited two unusual photophysical properties, strong photo-luminescence and dramatic increase in magnetization under UV irradiation at room temperature.

The EuO has localized narrow 4f orbitals existing as the degeneracy levels between the conduction band (5d orbitals of Eu(II)) and the valence band (2p orbitals of O^{2-}). The 4f–5d electron transition and spin configuration of EuO leads to unique optical-magnetic properties. The photo-magnetic phenomena have been described as "photo-magnetic polaron" in the theoretical field [6]. The theoretical approach of photo-magnetic polaron has been reported [7]; however, the spectral evidence of photo-magnetic polaron has never been observed. In this paper, we will report magnetic properties and the spectral analysis of the photo-magnetic phenomena of EuO nanocrystals using magnetization and electron paramagnetic resonance (EPR) measurements. Especially, "photo-magnetic polaron" will be discussed based on the EPR measurements.

2. Experiment

2.1. Preparation of EuO nanocrystals

The EuO nanocrystals were prepared in a N_2 atmosphere as follows: in a quartz vessel, $Eu(NO_3)_3$ (37.5 mM) and urea (112.5 mM) were dissolved in methanol (400 ml), then the solution was irradiated with a 500 W high-pressure mercury arc lamp at 25 °C. A yellowish powder precipitated after 30 min. After 24 h irradiation, the powder was separated by centrifugation and the resulting powdery precipitates were washed with methanol several times.

* Corresponding author. Tel.: +81 6 6879 7925; fax: +81 6 6879 7875.
** Co-corresponding author.
E-mail address: ywada@mls.eng.osaka-u.ac.jp (Y. Wada).

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2.2. TEM measurements

High-resolution images of the EuO nanocrystals were obtained with a Hitachi H-9000 transmission electron microscopy (high-resolution TEM) equipped with a tilting device (±10°) and operating at 300 kV (C_s = 0.9 mm). The TEM image of the initial EuO was fuzzy, but all TEM bright field (BF) images of EuO nanocrystals agreed with those of corresponding TEM centered dark-field (CDF) images, in which the incident beam was tilted such that the scattered beam remained on-axis. TEM observation revealed that the sample consisted of EuO nanocrystals with an average diameter of 3.4 nm. The electron diffraction patterns of the initial nanocrystals revealed responses at 2.95, 2.43, 1.78 and 1.51 dA, corresponding to (1 1 1), (2 0 0), (2 2 0) and (2 2 2) planes of NaCl-type EuO.

2.3. Characterization

Magnetization measurements verified the formation of Eu^{III}-free Eu^{II} oxides (EuO). TGA-DTA analysis indicated that the EuO precipitates contained 48% organic compounds. The elemental analyses combined with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) gave the empirical formula of the precipitates prepared in the absence and presence of urea, $Eu_1H_{6.7}C_{2.8}N_{1.2}O_{6.9}$ and $Eu_1H_{7.7}C_{3.3}N_{2.2}O_{6.8}$, respectively. The empirical formula of the organic component was determined from the balance between the empirical formula to be CH_2N_2. As the removal of H_2O (water) from NH_2–CO–NH_2 (urea) leaves CH_2N_2, the formation of polyurea $(–NH–CO–NH–CH_2–)_n$ on the surface of the EuO was anticipated. IR analysis verified the formation of polyurea did in fact occur.

2.4. Magnetic measurements

Magnetic susceptibility χ of EuO nanocrystals was measured using a superconducting quantum interface device (SQUID: Quantum Design, MPMS) magnetometer. Temperature dependence of $1/\chi$ of EuO nanocrystals was measured under field-cooled conditions at 0.1 T in darkness. Temperature dependence of χ was measured under field-cooled conditions at 0.1 T in darkness (circle). Samples were also irradiated (low-pressure mercury lamp: 256 nm) via optical fibers in magnetization measurement (triangle). SQUID measurements of conventional EuO without polyurea did not show enhanced magnetization under irradiation.

2.5. EPR measurements

The EuO nanocrystals were introduced into the EPR cell with Ar gas. The ESR spectra of the EuO nanocrystals were recorded on a JEOL JES-FA100 spectrometer under irradiation of a high-pressure mercury lamp (USH-1005D) focusing at the sample cell in the ESR cavity at 298 K. The magnitude of modulation was chosen to optimize the resolution and signal-to-noise (S/N) ratio of the observed spectra under non-saturating microwave power conditions. The g values were calibrated using an Mn^{2+} marker.

3. Results and discussion

3.1. Photo-magnetic measurements

The temperature dependencies of magnetic susceptibility χ of the EuO nanocrystals are shown in Fig. 1. These

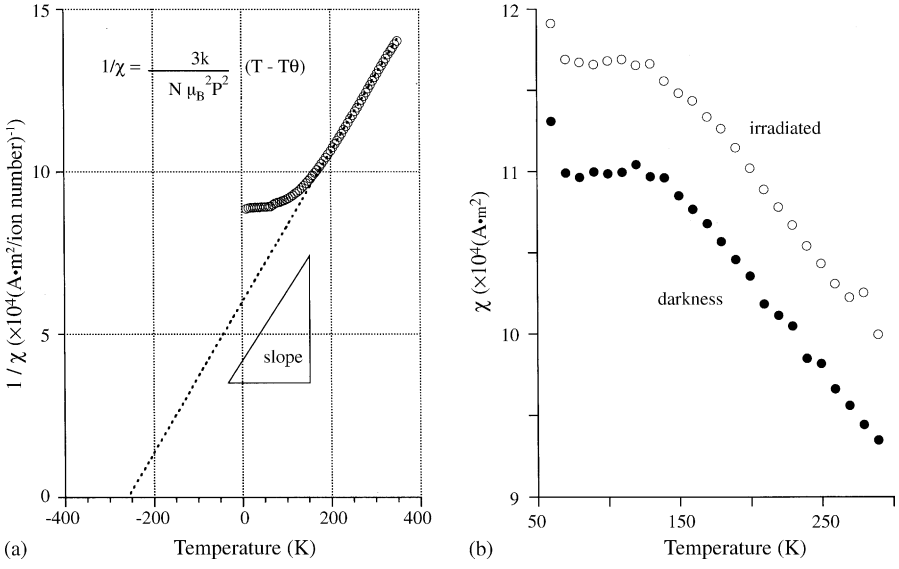

Fig. 1. (a) Temperature dependence of $1/\chi$ of EuO nanocrystals measured under field-cooled conditions at 0.1 T in darkness. (b) Temperature dependence of c measured under field-cooled conditions at 0.1 T in darkness (●), samples were also irradiated (low-pressure mercury lamp: 256 nm) via optical fibers in magnetization measurement (○).

magnetic properties were different significantly from those of corresponding EuO bulkcrystals. EuO nanocrystals show the super-paramagnetic properties because of difference from Curie–Weiss rule. The blocking temperature of EuO nanocrystal with polyurea was around 150 K. Previously, Kasuya and Yanase reported that the Curie temperature of bulk EuO was 80 K [6]. The Curie temperature is strongly increased by the oxygen vacancies or impurity state in the EuO crystal [8,9]. We also reported the Curie temperature of spindle-type EuO sub-microcrystal was found to be 150 K [10]. The Curie point agrees with the value reported for EuO thin films with oxygen vacancies [9]. The number of oxygen vacancies of EuO nanocrystals would be as high as that of EuO sub-microcrystals. We propose that the blocking temperature around 150 K is due to the presence of lots of oxygen vacancies on the EuO surface.

We calculated the electron configuration of the EuO nanocrystal by using SQUID measurements. The T versus $1/\chi$ asymptote is given by,

$$\frac{1}{\chi} = \frac{3k}{N\mu_B^2 P^2}(T - T_\theta), \quad (1)$$

where T_θ, χ, μ_B, N and P are Curie–Weiss temperature, magnetic susceptibility, Bohr magnetic moment (9.274×10^{-24} J/T), Boltzmann constant (1.38066×10^{-23} J/T), number of Eu ions in the sample and effective Bohr magneton, respectively. From the slope of the T versus $1/\chi$ asymptote of the EuO nanocrystals ($3k/[N_B^2 p^2]$), the experimental effective number of Bohr magnetons (p) for the EuO nanocrystals was found to be 7.98.

On the other hand, the theoretical p is given by,

$$p = g\sqrt{J(J+1)}, \quad (2)$$

where g and J are constant ($g = 2.0023$) and total angular momentum (J value of Eu(II): 7/2). The theoretical effective number of Bohr magnetons for Eu(II) was found to be 7.94. The experimental p for EuO nanocrystals agreed well with the theoretical p for the $4f^7$ configuration (Eu(II)).

A dramatic increase in magnetization of the EuO nanocrystals under UV irradiation at room temperature was observed by photo-magnetic measurements (SQUID with optical fiber). The T–χ curve of the EuO nanocrystals under irradiation was shifted towards the high χ value from that of EuO in darkness (Fig. 1b: circle). On the other hand, SQUID measurements of EuO nanoparticles without polyurea (average size = 4 nm) did not show enhanced magetization under irradiation. This increase in magnetization under UV irradiation can be explained by the occurrence of a d–f exchange interaction of conductive electrons in the 5d band [7]. The magnetization measurement for Fig. 1 is based on the pure magnetic physics, as reported in the previous papers [11]. We suggest that the mechanism of the magnetization increase may be attributable to the presence of an exciton band in the UV region in accordance with the highly efficient luminescence from the polyurea-modified EuO nanocrystals. The photo-magnetic response of quantum-sized EuO nanocrystals with exciton would support the physical theory of the magnetic exciton model with super-interaction between spins in 5d band and 4f orbitals, experimentally [6]. The exciton bands should be concerned with the excited electron in the d orbital and is in good agreement with the understanding of the photo-magnetic properties. The special interaction between d and f orbitals, i.e. the photoinduced localized magnetic exciton bound by the 4f hole produced in the photoexcitation is acceptable as reported for EuTe in the precedent paper [7]. A conceptual image of photo-magnetization increase is shown in Fig. 2. We suggest that the mechanism of the photo-magnetization increase is attributable to the presence of an exciton band in the UV from the polyurea-modified EuO nanocrystals.

3.2. EPR measurements

The EPR spectra of EuO nanocrystals depending on the temperature are shown in Fig. 3a. The EPR spectral shape of EuO nanocrystals were similar to that of reported EuO ($g = 2.01$) [12]. On the other hand, experimental p value introduced g constant (2.003) was agreeable with theoretical p for the magnetic measurements. The EPR spectral signal of EuO nanocrystals might correspond to the data from the magnetic measurements. The sharp signal at 330.5 mT was assigned to organic radical species, indicating the presence of some organic radical species on the EuO surface. This organic radical species would be produced during the formation of EuO nanocrystals under UV irradiation, in which methanol radical plays a key role [5]. Integration curves of the EPR spectra are shown in Fig. 3b. The signal intensities of the integration curves increased with decreasing of temperature. The full width at half maxim (FWHM) of the integration curve at 113 K (dash line in Fig. 3a and b) was different from those of corresponding the integration curves at 153, 193 and 273 K. In order to confirm the magnetic exciton of EuO nanocrystals, we carried out the EPR measurements under UV irradiation at 273 K. The difference spectrum was calculated by subtraction of the integration curve in darkness from that under corresponding UV irradiation. The integration curves and difference spectrum are shown in Fig. 4. The area of the integration curve of EuO nanocrystals under UV irradiation was larger than that of EuO nanocrystals in darkness at 273 K. The peak top of differential spectrum was found to be 300 mT and was different from those of corresponding Eu(II) signals (210–220 mT).

The EPR signal of the EuO nanocrystals changes under 130 K. It seems that the alteration is due to the change of the magnetic state of the Eu(II) nanocrystals [12]. We observed that the blocking temperature of EuO nanocrystal with polyurea was around 150 K. The EPR signal under 130 K might be affected by the magnetic state of EuO nanocrystals. In Fig. 3, decrease of the FWHM of the inte-

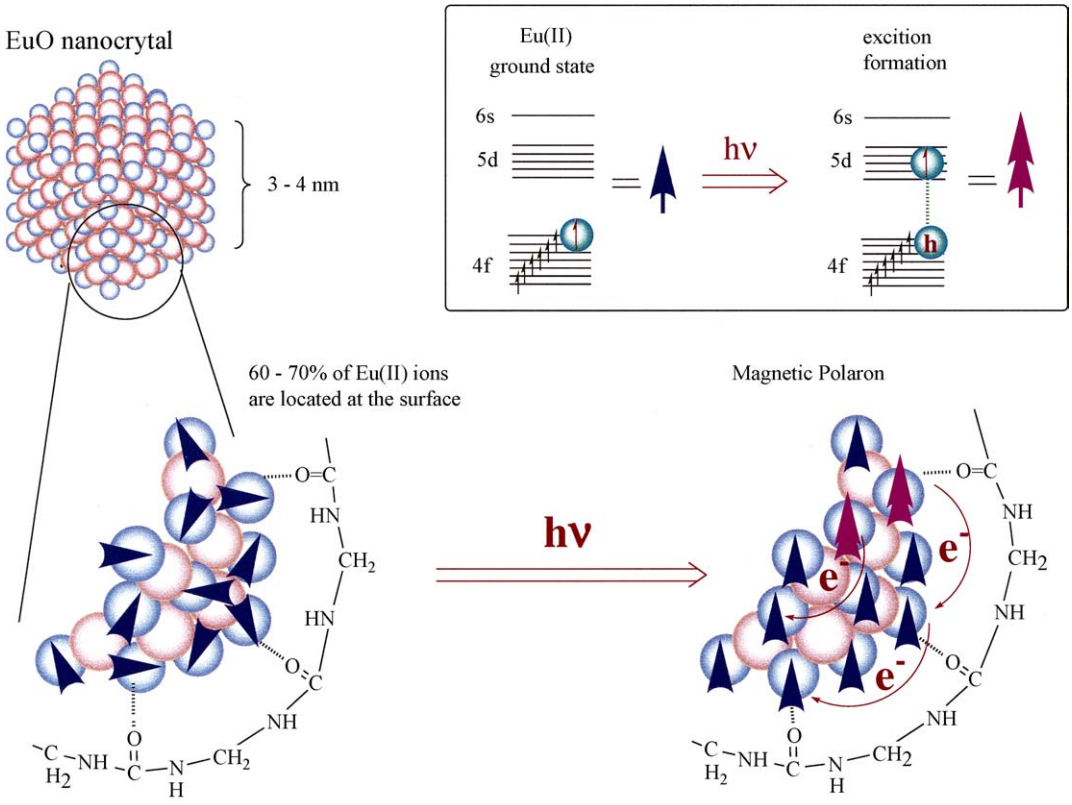

Fig. 2. Conceptual images of photo-magnetic polaron.

gration curve at 113 K corresponds to the transformation of the magnetic property of the EuO nanocrystals. Furthermore, integration curves of EPR spectrum under irradiation (Fig. 4) would show the formation of photo-active spins in EuO nanocrystals. We propose that the difference spectrum in Fig. 4 might be linked to increase of magnetic susceptibility of EuO nanocrystals under UV irradiation and photo-magnetic polaron. We are now trying to observe some more direct evidence of the photo-magnetic polaron of EuO nanocrystals.

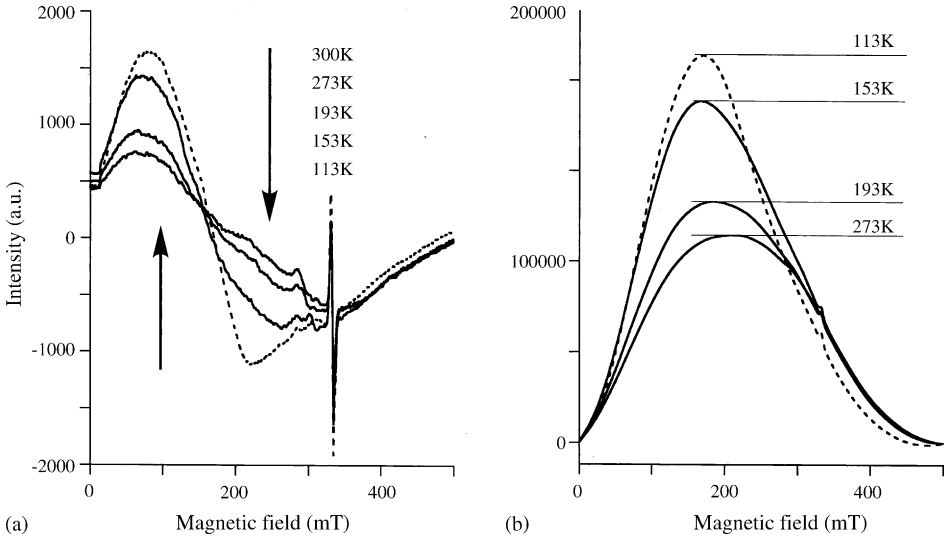

Fig. 3. Temperature dependencies of EPR signals of EuO nanocrystals. The spectra of the graph (b) (bold lines: at 153, 193 and 273 K, dash line: at 113 K) are integration curves of EPR signals of graph (a).

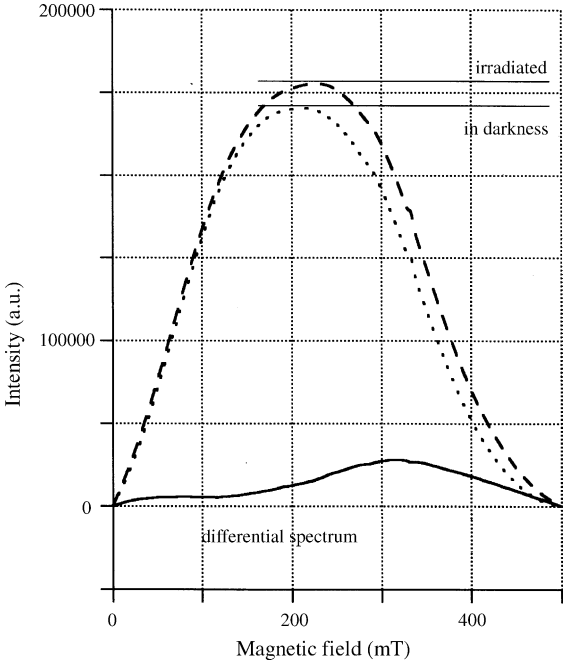

Fig. 4. Integration spectra of EPR signals of EuO nanocrystals under irradiated (dot line), in darkness (dash line) and differential spectrum (bold line).

4. Conclusions

We observed increase in magnetization of EuO nanocrystal with polyurea using SQUID under irradiation. EPR spectrum under irradiation proposes the formation of photoactive spins in EuO nanocrystals. In order to understand the photo-magnetic phenomena, quantitative magnetic analyses would be needed. The quantitative magnetic analyses are expected to clear the mechanism of the photo-magnetic polaron. EuO nanocrystals would be highly useful in future organic–inorganic hybrid devices, such as plastic photoisolators, opto-magnetic memory disks. The EuO nanocrystals and this novel synthesis are expected to open up pioneering fields of functional rare-earth semiconductor, not only for magnetic materials, but also for photo-magnet data conversion devices.

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