



Local structures and magnetic properties of Fullerene–Co systems studied by XAFS and XMCD analyses

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ABSTRACT

In this work we have measured Co K- and L_{2,3}-edge X-ray absorption near edge structure (XANES) and Co L_{2,3}-edge X-ray magnetic circular dichroism (XMCD) spectra, and also carried out their calculations for C₆₀Co_x compounds. The observed XANES and XMCD are sensitive to the Co concentration. In the low density region ($x = 1.0 - 1.5$), one Co is surrounded by three C₆₀ balls. The Co L_{2,3}-edge XMCD analyses gives the spin magnetic moment on Co in the range 0.5–0.9 μ_B .

In the high density region ($x = 4.0 - 4.3$) calculated XANES for one of the proposed model, 4C₆₀–4Co model, by Nakajima and Kaya give rather good agreement with the observed XANES, where a Co₄ cluster is surrounded by four C₆₀ balls. Fourier transformed extended X-ray absorption fine structure (EXAFS) is well explained by this model. In contrary to these results, the calculated XMCD spectrum for that high-symmetric model shows rather poor agreement with the observed spectrum. Lowering the symmetry, we can improve the agreement. The cluster density functional calculations for the 4C₆₀–4Co model show that spin quintet (4 μ_B) is in the lowest energy. Each Co has 1 μ_B in ferromagnetic like order. The results also indicate that the band gap for the minority spin is smaller than that for the majority spin. This result provides us with fundamental information to understand the tunnel magnetoresistance (TMR) mechanism in those systems.

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1. Introduction

Conventional electronics depends on the manipulation of charge. The information processing is moving from control of charge to spin. Spin has long been used to hold information; dynamics of aligned spin form bits in magnetic recording. In spintronics, packets of spin travel through wire, carrying bits now as packets of charge do. Inorganic materials are widely used as spin-storage and -transport media, however molecular spintronics are expected to have significant advantages over those inorganic systems because of long spin-relaxation time and spin-diffusion length [1–3]. Among them, magnetotransport properties were investigated for codeposited C₆₀–Co films by Sakai et al., who found at low temperature a giant tunnel magnetoresistance (TMR) ratio $\Delta R/R_{max}$ of 80–90% (the highest in ferromagnetic metal/organic molecules) [4]. Very recently the TMR effect of granular C₆₀–Co films at low temperature and also at small applied voltages is studied in the current-perpendicular to plane geometry to elucidate the

spin-dependent tunneling process [5]. However, the mechanism of these MR effects have not been clarified in detail because of limited information about electronic and spin states essential for the magnetotransport properties.

The structures of the C₆₀–Co_x films are classified into two regions: the Co-dilute region ($x < 5$) consisting of a homogeneous compound and the Co-dense region ($x \geq 5$) with a granular structure. According to the results on the microstructure evolution depending on Co content (C₆₀Co_x, x : the number of Co atoms per a C₆₀ molecule) [6,17], in the Co-dilute region, (C₆₀)_n–Co cluster is formed; the detailed information on the local structure and the coordination number of Fullerenes n have not been obtained. In the Co-dense region ($x \geq 5$) dispersing Co nanoparticles are generated in the C₆₀–Co compounds [6]. Matsumoto et al. have applied X-ray absorption fine structure (XAFS) spectroscopy and X-ray magnetic circular dichroism (XMCD) to the C₆₀–Co_x films in order to study the electronic and spin states of these systems in the region ($4.3 < x < 13.4$) [7]. They observe paramagnetic-like spin polarization with spin moment 0.5 μ_B for C₆₀Co_{4.3}. The small orbital moment <0.05 μ_B is considered to be induced by the formation of C–Co bonds. In the Co-dense region ($x > 5$), the XMCD intensity increases with x . The estimated spin and orbital moments

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are $1.35 \pm 0.30 \mu_B$ and $0.16 \pm 0.07 \mu_B$. The local structures of related systems have been investigated. For example, in K_3-C_{60} , C_{60} units form fcc cell and K atoms occupy the center of tetrahedrons and octahedrons [8]. The structure of Cs_6-C_{60} [9] and Ca_5-C_{60} [10] has also been studied.

To obtain the more detailed information on structures, electronic and spin states of these systems, more detailed experimental and more sophisticated theoretical analyses are necessary. In this paper we thus apply relativistic multiple scattering theory to study these problems.

2. Experimental

Details of the experiments were described elsewhere [7,18], but brief description is only shown here for the later discussion in this paper. Measurements of Co $L_{2,3}$ -edges X-ray absorption near edge structure (XANES), X-ray magnetic circular dichroism (XMCD) spectra and Co K-edge XANES spectra of the C_{60} -Co compounds ($C_{60}Co_x$, $x < 5$) were carried in the total-electron-yield mode at BL4B of UVSOR-II (IMS) and BL7A of Photon Factory (KEK) and in the fluorescence mode at BL27A of Photon Factory (KEK), respectively. 30 nm thick $C_{60}Co_x$ films grown on Ag/MgO(001) substrates were utilized for the $L_{2,3}$ -edges XANES and XMCD measurements at 6K by transferring the samples from an ultra-high vacuum (UHV) sample-preparation chamber to the analysis chamber without breaking UHV. The Co $L_{2,3}$ -edges XMCD spectra were obtained by reversing the magnetic field (± 50 kOe) parallel and antiparallel to the propagating direction of the circularly polarized X-ray. 100 nm thick $C_{60}Co_x$ films capped with a 150 nm thick SiO layer were utilized for the K-edge XANES measurements at ambient temperature under a nitrogen atmosphere.

3. XAFS and XMCD theory

The XAFS and XMCD theory used in this paper is based on the one-electron relativistic multiple scattering theory developed by the authors [11–13]. The 4-spinor core state $|\chi_c\rangle$ can be written in terms of large component $|\varphi_c\rangle$ and the small component $|\chi_c\rangle$. By using full relativistic Green's function G_D , the X-ray absorption intensity is described by

$$I(\omega) = -2\text{Im}\langle c | H_{ep} G_D(\varepsilon) H_{ep} | c \rangle \quad (3.1)$$

where ε is the kinetic energy of photoelectrons, and H_{ep} is the electron-photon interaction Hamiltonian. The full relativistic formula (3.1) is expanded up to the relativistic order [14,15]

$$I(\omega) = T_{11}(\omega) + T_{12}(\omega) + T_{21}(\omega) + U_{11}(\omega) + \dots \quad (3.2)$$

where T_{11} is the most important term which neglects the relativistic effects on photoelectrons but includes them in the core function φ_c

$$T_{11}(\omega) = -2\text{Im}\langle \varphi_c | \Delta_{m_p}^* g(\varepsilon) \Delta_{m_p} | \varphi_c \rangle. \quad (3.3)$$

The one-electron dipole operator Δ_{m_p} reflects the incident X-ray polarization, $\Delta_{m_p} \propto Y_{1m_p}(\hat{\mathbf{r}})$ ($m_p = 0, \pm 1$). The Dirac Green's function G_D is now replaced by the nonrelativistic full one-electron Green's function g . In case of $L_{2,3}$ edge XAFS and XMCD analyses, it is sufficient to take the T_{11} term into account. The XANES spectra can be calculated by use of Eq. (3.3) with $m_p = 0$, and the XMCD spectra ΔT_{11} can be calculated by

$$\Delta T_{11}(\omega) = -2\text{Im}[\langle \varphi_c | \Delta_1^* g(\varepsilon) \Delta_1 | \varphi_c \rangle - \langle \varphi_c | \Delta_{-1}^* g(\varepsilon) \Delta_{-1} | \varphi_c \rangle]. \quad (3.4)$$

For nonmagnetic systems, the XMCD vanishes whereas it is finite for magnetic systems because of spin-dependent exchange scatterings. XANES spectra are calculated by use of Eq. (3.3) for the linear polarization $m_p = 0$ [16].

When the $2p_{1/2}$ and $2p_{3/2}$ core levels are degenerate, we have to take sum over μ for $j_c \mu$ ($j_c = 1/2, 3/2$) sublevels. For the nonmagnetic systems they are degenerate, but for the magnetic systems they are splitted into two ($2p_{1/2}$) and four ($2p_{3/2}$) core levels because of the exchange interaction between the spin polarized $3d$ electrons and the core electrons in the relativistic sublevels. So far we have calculated XMCD spectra neglecting the core level splitting: we simply calculate the sum over c in Eq. (3.4). In this work in addition to these simple calculations we show a result considering the exchange effect. Based on Unrestricted Hartree-Fock (UHF) theory, we can estimate the exchange energy contribution to the UHF core orbital energy of $\varphi_{j\mu}$

$$-\sum_{mm_s} n_m^{m_s} K_{m\mu} = -\sum_{mm'} (n_m^+ K_{mm'}^+ \langle 1m'1/2, 1/2 | j\mu \rangle^2 + n_m^- K_{mm'}^- \langle 1m'1/2, -1/2 | j\mu \rangle^2) \quad (3.5)$$

where n_m^\pm is the occupation number at $3d_m$ orbital with \pm spin, $K_{mm'}^\pm$ is the exchange integral between electrons in $3d_m$ and $2p(j\mu)$ orbitals.

The systems considered here have quite small orbital moment, and the present approaches which neglect detailed atomic multiplet effects would not have serious problems.

4. Fullerene-Co $_x$ ($x = 1.0 - 1.5$)

In this Co-dilute region, useful structural information on C_{60} -Co $_{2.9}$ has been obtained by use of the Co K-edge EXAFS [17,18]. The nearest Co-C distance is 2.01 Å with coordination number 6 and the second nearest one is 3.15 Å. A quantum chemical study using the *ab initio* density functional theory (DFT) shows that the η^2 (6-6 edge of C_{60}) type of Co ion coordination is preferable for $(C_{60})_m Co_n$ ($n = 1$ and 2) clusters [19]. Similar result is also obtained by Javan et al. [20].

Referring to these results, we investigate the two plausible models (a) Co-2 C_{60} [η^2/η^2] and (b) Co-3 C_{60} [$\eta^2/\eta^2/\eta^2$] shown in Fig. 1. The DFT calculations give slightly shorter Co-C nearest distance than the EXAFS result for the model (a), and slightly longer for the model (b). We thus adjust the nearest Co-C distance to be 2.01 Å keeping the shape of the calculated models. Thus the second nearest Co-C distance is 3.07 Å with 8 coordinated C for the model (a), and 3.04 Å with 12 carbons for the model (b). These distances are comparable with the EXAFS result [17]. Fig. 2 shows the calculated Co $L_{2,3}$ -edge XANES spectra for these models (a) 2 C_{60} -Co and (b) 3 C_{60} -Co. The observed L_3 -edge XANES shows a shoulder at lower energy side, whereas L_2 -edge XANES shows a broad single peak. The calculated L_3 -edge XANES for the model (a) shows a shoulder but at higher energy side, which is against the observed result. The one for the model (b) shows a shoulder at lower energy side, which is in agreement with the observed behavior. The both models give a broad peak at L_2 -edge region. This result predicts that the model (b) is preferable. The DFT calculations also support the model (b) which has the lowest energy among the models studied there [19]. The EXAFS result (coordination number 6) [18] also prefers the model (b) because of the coordination number 6 in the model (b), but 4 in the model (a); the experimental result is 6. Fig. 3 shows the Co K-edge XANES compared with the calculated spectra for the models (a) and (b) shown in Fig. 1. We again obtain the better result for the model (b), since the model (a) gives the doublet structure whereas the model (b) gives only a broad peak.

Next we discuss the magnetic structure of the 3 C_{60} -Co model. We assume that the cluster is neutral with spin doublet (low spin) or spin quartet (high spin). The DFT calculations by use of Gaussian code (B3LYP 6-31G basis) [21] show that the low spin configuration is more stable than the high spin state. The energy difference

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