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Description	

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Crystal structure and electronic transport of Dy@C$_{82}$

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The crystal structure of Dy@C$_{82}$ isomer I at 298 K has been determined by Rietveld refinement for x-ray powder diffraction with synchrotron radiation. Isomer I shows a simple cubic structure (sc: $Pa\overline{3}$) with a lattice constant a of 15.78(1) Å. The C$_2$ axis of a C$_{2v}$-C$_{82}$ cage aligns along the [111] direction of this crystal lattice. The C$_{82}$ cage is orientationally disordered to satisfy a $\overline{3}$ symmetry along [111], which is requested in this space group. The large thermal parameter for the Dy atom estimated from the x-ray diffraction probably reflects a large disorder caused by a floating motion of the Dy atom inside the C$_{82}$ cage as well as a ratchet-type motion of the Dy@C$_{82}$ molecule. The electronic transport of thin film of Dy@C$_{82}$ shows a semiconducting behavior. The energy gap E_g is estimated to be 0.2 eV. Further, the variation of valence from Dy^{3+} to Dy^{2+} is found by metal doping into the Dy@C$_{82}$ crystals.

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INTRODUCTION

Structures and transport properties of solid metallofullerenes (M@C$_n$) are a very exciting research-subject in chemistry and physics. The crystal structure of M@C$_n$ was first determined by a maximum entropy method (MEM) analysis for x-ray powder diffraction of crystalline solid of 1:1 toluene-solvate of Y@C$_{82}$.[1] The crystals were assigned to a monoclinic space group of $P2_1$, and the Y atom lay on a six-membered ring inside the C$_{82}$ cage. Further, the MEM analysis was applied to the structural determination of 1:1 toluene solvates of Sc@C$_{82}$ and Sc$_2$@C$_{84}$; the space group was $P2_1$ for both crystals.[2,3] The crystal structure of solvent-free M@C$_n$ was determined with single crystals of La@C$_{82}$ isomer I by Watanuki *et al.*[4] The crystals of La@C$_{82}$ isomer I take a face-centered-cubic (fcc) lattice with a lattice constant a of 15.78 Å at 300 K. The structural transitions to various phases were found in a wide temperature region from the x-ray diffraction for single crystals of La@C$_{82}$ isomer I.[4,5] The various phases are realized by differences in the molecular orientation of the C$_{82}$ cage and the molecular electric dipole moment produced by a displacement of metal ion from the cage center. The magnetic property of a La@C$_{82}$(CS$_2$)$_{1.5}$ solid with a body-centered-cubic (bcc) structure ($I\overline{4}3d$) was recently reported by Nuttall *et al.*[6] In crystals, the long axis of the C$_{82}$ cage is oriented along the [111] direction and the La atom is displaced along [111] from the center of the C$_{82}$ cage.[7] The magnetic property shows a strong antiferromagnetic interaction (a Weiss temperature $\theta\sim-130$ K).[6] A phase transition was observed at 150 K, which originates from an orientational ordering of the C$_{82}$ cage. Further, two crystal structures were reported for Ce@C$_{82}$ by Nuttall *et al.*[8] The crystals obtained after an annealing under vacuum take a hexagonal-close-packing (hcp) structure ($P6_3/mmc$, $a=11.1544$ Å and $c=18.2256$ Å), while the sublimated Ce@C$_{82}$ crystals dominantly take a fcc lattice ($Fm\overline{3}m, a=15.766$ Å), and include the hcp phase as a minor phase. The x-ray powder diffraction patterns show a drastic variation between the two crystal structures.

We reported on the x-ray powder diffraction and the x-ray Absorption Fine Structure of a purified sample of solvent-free Dy@C$_{82}$ which contains at least two isomers of I and II.[9] The x-ray diffraction pattern of mixed crystals of isomers I and II at 298 K were indexed with an fcc lattice of $a=15.86(1)$ Å. The x-ray absorption near-edge structure (XANES) of the Dy@C$_{82}$ sample revealed a valence of +3 for the Dy atom. The distance between the Dy atom and the first nearest C atoms, C(1), and that between the Dy atom and the second nearest C atoms, C(2), were determined to be 2.52(2) and 2.86(2) Å, respectively, from an extended x-ray-absorption fine-structure (EXAFS). Very recently, we found a structural phase transition from sc to fcc for solvent-free crystals of Dy@C$_{82}$ isomer I around 310 K based on the temperature dependence of the lattice constant and peak intensities of the x-ray diffraction ascribable to the sc phase.[10] This structural phase transition was confirmed by a differential scanning calorimetry. Therefore, the crystals of isomer I take a sc structure at 298 K, although the mixed crystals were assigned to the fcc structure.

The transport properties of metallofullerenes are very important and interesting research-subject because they give a key for their application to electronic devices. The resistivity ρ of single crystals of La@C$_{82}$ was measured by a two-probe method.[11] The La@C$_{82}$ crystals were a small gap semiconductor with gap energy, E_g, of 0.3 eV. The photoemission spectrum of La@C$_{82}$ also showed an E_g of 0.35 eV for La@C$_{82}$.[12–14] Very recently, the optical gap of 0.3 eV was observed in the absorption spectrum of a thin film of La@C$_{82}$.[15] The transport properties for the solid samples of metallofullerenes except for La@C$_{82}$ have never been studied, to our knowledge.

In the present paper, the crystal structure of a Dy@C$_{82}$

isomer I in the sc phase is determined by Rietveld refinement for x-ray powder diffraction. The orientation of the C_{82} cage and the Dy atom in the unit cell are discussed. Further, the electronic transport property is studied by a ρ measurement for a thin film of Dy@C_{82}, and a semiconducting behavior is observed below 350 K. Finally, the intercalation of K atoms with the Dy@C_{82} crystals is tested, and a variation of valence from Dy^{+3} to Dy^{+2} is observed.

EXPERIMENT

Details for the separation of Dy@C_{82} isomer I was described elsewhere.[9] The characterization of the isomer I was performed by a high performance liquid chromatography, time-of-flight (TOF) mass spectra, and the UV-VIS-NIR absorption spectra. The molecular symmetry of isomer I was identified to be C_{2v} from the similarity in the UV-VIS-NIR spectrum to those of La@C_{82} isomer I and Pr@C_{82} isomer I.[9,16–20] Further, the UV-VIS spectrum of Dy@C_{82} isomer I obtained by our group was consistent with that of the Dy@C_{82} isomer of C_{2v} cage symmetry reported by Tagmatarchis and Shinohara.[18] The solid sample of isomer I was obtained by evaporating toluene from the toluene solution of isomer I separated after five-step HPLC. A trace of toluene was removed from the solid sample by a dynamical pumping under a pressure of 10^{-6} Torr for 12 h at room temperature, for 12 h at 473 K, and for 48 h at 573 K. A solvent-free solid sample was introduced, without exposure to air in an Ar glove box, into a glass capillary ($\phi = 0.5$ mm) for an x-ray-diffraction measurement. The x-ray powder diffraction patterns of the isomer I were measured at 119 and 298 K under ambient pressure (1 bar) [wavelength $\lambda = 0.8520(1)$ Å] at BL-1B of KEK-PF (Tsukuba, Japan).[21] The ρ of the thin film of Dy@C_{82} was measured from 170 to 350 K by using four-probe methods. Dy@C_{82} was deposited on Au electrodes 56 nm thick, and 5000 μm wide, and a 20-μm channel distance was formed on the SiO_2/Si substrate at a deposition rate of 0.01 nm s^{-1} under a pressure of $\sim 10^{-6}$ Torr; the thickness of SiO_2 was 570 nm. The thickness and width of the Dy@C_{82} thin film were 120 nm and 3000 μm, respectively. The K_xDy@C_{82} sample was prepared by annealing K metal and Dy@C_{82} in a glass tube under a vacuum of 10^{-5} Torr at 450 °C for 20 days; an excess K metal was added to Dy@C_{82} in the glass tube. The sample was introduced into a glass capillary in an Ar glove box for XANES measurement. The XANES spectra of Dy@C_{82} and K_xDy@C_{82} were measured at 298 K in a fluorescence mode at BL-12C of KEK-PF.

RESULTS AND DISCUSSION

Crystal structure of Dy@C_{82} isomer I

The x-ray-diffraction pattern of isomer I at 298 K can be indexed with an sc lattice of $a = 15.78(1)$ Å, as shown in Fig. 1. The *hkl* reflections do not satisfy the condition of $h+k$, $h+l$, $k+l=2n$ for *hkl*, although the reflections without the condition are weak. All x-ray powder diffraction patterns for isomer I from 17 to 298 K at 1 bar can be indexed with the sc lattice, as reported previously.[10] We enumerated all space groups, $Pm\bar{3}$, $Pn\bar{3}$ $Pa\bar{3}$, $P2_13$ and $P23$, which satisfy the condition that there are four Dy@C_{82} molecules per one conventional cubic cell, in the same manner as the solvent-free fcc La@C_{82} crystals.[4]

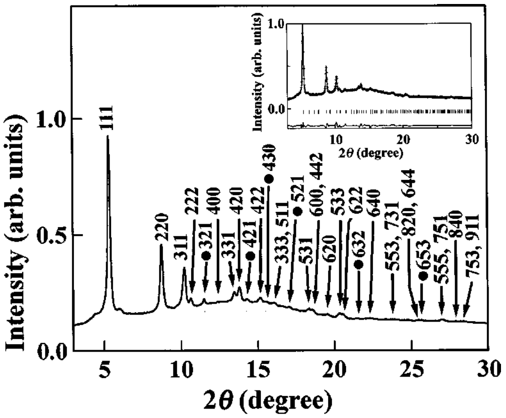

FIG. 1. Observed x-ray-diffraction pattern (solid line) of the Dy@C_{82} isomer I at 298 K together with indices for a sc lattice. The symbols ● show the peaks which cannot be indexed with a fcc lattice. In the inset, the observed x-ray-diffraction pattern (+ symbols) and that calculated with the structural parameters determined by Rietveld refinement (solid line). The allowed peak positions and the difference between the observed and the calculated patterns are drawn by ticks (middle) and the solid line (bottom), respectively.

If an inversion symmetry is assumed for the crystal structure, three possible space groups of $Pm\bar{3}$, $Pn\bar{3}$, and $Pa\bar{3}$ can be suggested. For the general position (24*h*) in $Pn\bar{3}$, the systematic absence is $k+l=2n$ for $0kl$ and $h=2n$ for $h00$. As indicated in Fig. 1, the existence of 430 reflection rules out the possibility of $Pn\bar{3}$. On the other hand, the observed reflections satisfy the systematic absence ($k=2n$ for $0kl$ and $h=2n$ for $h00$) for the general position (24*d*) in $Pa\bar{3}$. Further, the general position (24*l*) in $Pm\bar{3}$ does not require any systematic absence. However, we performed the Rietveld refinement for the x-ray powder diffraction pattern based on all these space groups because the 430 reflection is weak.

The C_{2v}-C_{82} cage of Dy@C_{82}, which posesses no $\bar{3}$ symmetry, has to be orientationally disordered because the symmetry 3 or $\bar{3}$ is required along [111] to realize a cubic crystal. At first, the refinement for the crystals of the Dy@C_{82} isomer I was carried out based on $Pa\bar{3}$. The crystals of $Pa\bar{3}$ are found for the low-temperature phase of pristine C_{60} and Na_2C_{60};[22,23] in the crystals, the six membered ring of the C_{60} molecule was faced to [111] to satisfy the $\bar{3}$ symmetry. In this case, the C_{60} molecule does not need orientational disorder because the molecule has a $\bar{3}$ symmetry. For the Dy@C_{82} isomer I, the center of C_{2v}-C_{82} cage was placed on the origin of the unit cell, and the C_2 axis of the C_{82} cage was aligned along [111]; such an orientation is found in the crystals of solvent-free La@C_{82} and La@$C_{82}(CS_2)_{1.5}$.[4,7] The C—C bond lengths in the initial C_{2v}-C_{82} cage were taken as 1.37–1.47 Å. The number of crystallographically independent C atoms is 82 in the $Pa\bar{3}$ unit cell because the C_{2v}-C_{82}

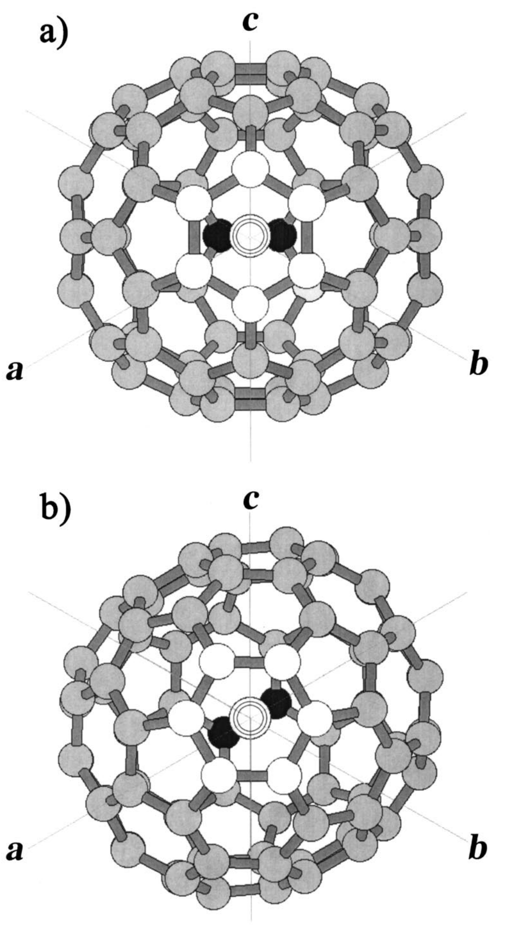

FIG. 2. Structure of C_{2v}-Dy@C_{82} molecule viewed along [111]. The setting angle ϕ is taken as $\phi = 0°$ for the structure shown in (a), and ϕ=30° in (b). The white and black circles refer to the C atoms in the closest six-membered ring to the Dy atom and those in the fused six-membered rings, respectively. The C_2 axis of the cage passes through the six-membered ring and the center of the fused six-membered rings. The triple circle refers to the Dy atom.

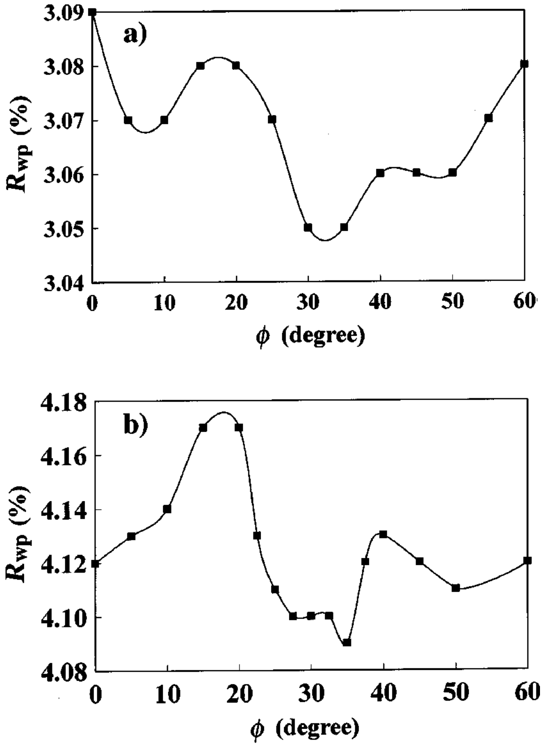

FIG. 3. Plots of R_{wp} calculated with the structure obtained by the Rietveld refinement for the x-ray-diffraction pattern at 298 K by assuming the space group of (a) $Pa\bar{3}$ and (b) $P2_13$ vs ϕ. R_{wp} refer to the values for the structure refined in the arbitrary ϕ, and are calculated at the ϕ denoted by the ■ symbols. The solid line is drawn by curve fitting.

has no $\bar{3}$ symmetry. All C atoms occupy 24d sites in the $Pa\bar{3}$ unit cell. The occupancy of the C atoms is 1/6. The Dy atom was initially placed on the C_2 axis of the cage with the Dy-C(1) distance of 2.52(2) Å determined by EXAFS, where the distance between the Dy atom and the cage center is 1.85 Å. (Ref. 9); the Dy atom occupies the 8c site with an occupancy factor of $\frac{1}{2}$. The structure of Dy@C_{82} viewed along [111] is shown in Figs. 2(a) and 2(b). The rotation of the cage around [111] is allowed in the crystals of $Pa\bar{3}$. Thus the Rietveld refinement is performed in the arbitrary setting angle ϕ around [111]. The geometrical structure of the C_{82} cage was fixed to the initial one, and x and the temperature factor B of the Dy atom were refined. Figure 3(a) shows plots of weighted pattern R factor R_{wp} vs ϕ. The R_{wp} curve shows two local minima at $\phi = 7.5°$ and 50°, and a global minimum at ϕ=30°, though the difference in the R_{wp} at each ϕ is very small.

The x-ray-diffraction pattern of Dy@C_{82} isomer I, and that calculated with the structural parameters at ϕ=30°, are shown in the inset of Fig. 1. The final R_{wp} and integrated intensity R factor R_I are 3.05% and 2.54%, respectively. The Dy-C(1) distance was 2.68(2) Å, which is larger than that, 2.52(2) Å, determined by EXAFS. The displacement of the Dy atom from the cage center is 1.64 Å. On the other hand, the x-ray-diffraction patterns calculated by assuming the space groups of $Pn\bar{3}$ and $Pm\bar{3}$ could not reproduce the experimental one, although the Rietveld refinements in various ϕ were examined. This result implies that the $Pn\bar{3}$ and $Pm\bar{3}$ can be ruled out from the candidates of the space group for the low-temperature phase of Dy@C_{82} isomer I.

Further, we tried to analyze the x-ray-diffraction data based on the space groups, $P2_13$ and $P23$, which have no inversion symmetry. At first, the Rietveld refinement was performed based on the space group of $P2_13$ which is a maximal subgroup of $Pa\bar{3}$. The procedure of the Rietveld refinement is the same as that for the space group $Pa\bar{3}$, except for the occupancy factors of C and Dy atoms which are 1/3 and 1, respectively. The plots of R_{wp} vs ϕ is shown in Fig. 3(b). The curve is similar to that for $Pa\bar{3}$. However, the R_{wp} value of 4.09% at global minimum for $P2_13$ is larger by ~1% than that for $Pa\bar{3}$. The difference of ~1% in R_{wp} between $Pa\bar{3}$ and $P2_13$ is significant because the number of

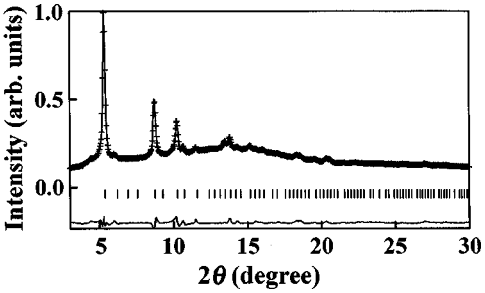

FIG. 4. Observed x-ray-diffraction pattern (+ symbols) at 298 K and that calculated with the structural parameters determined by Rietveld refinement (solid line); the Dy atom is displaced from the C_2 axis of the C_{82} cage. The allowed peak positions and the difference between the observed and calculated patterns are drawn by ticks (middle) and the solid line (bottom), respectively.

parameters are the same in both space groups. Consequently, the space group $Pa\bar{3}$ is supported, whose space group is the same as that for pristine C_{60}.[22] Further, we tested the space group $P23$, which is a maximal subgroup of $Pn\bar{3}$ and $Pm\bar{3}$. However, the experimental x-ray-diffraction pattern could not be reproduced with this model. Therefore, we have excluded these models with no inversion center.

The value of B, 132(24) Å^2, of the Dy atom determined by the Rietveld analysis in the space group of $Pa\bar{3}$ is extremely large. This suggests a disorder of the Dy atom around [111]. This type of disorder is allowed in the crystals of $Pa\bar{3}$. We tried to displace the Dy atom from the C_2 axis of the C_{82} cage. The position of the Dy atom was changed from the site $8c$ to the $24d$ site; the occupancy of the Dy atom was set to $\frac{1}{6}$. The Dy atom was initially displaced by 0.6 Å from the C_2 axis. The Rietveld refinement was performed at $\phi = 30°$; here the geometry of the C_{82} cage was fixed to the initial one, and the parameters (x, y, z) and B of the Dy atom were refined. The x-ray-diffraction pattern obtained by the Rietveld refinement is shown in Fig. 4; R_{wp} and R_I are 2.91% and 2.07%, respectively. The B value was estimated to be 25(7) Å^2. The decrease in B by displacing the Dy atom from the C_2 axis implies a large disorder of the Dy atom in Dy@C_{82}. Very recently, a displacement of the Tm atom from the C_2 axis in Tm@C_{82} is found from EXAFS below 20 K, which is very small in comparison with that in Dy@C_{82}.[24]

The Dy@C_{82} molecule takes place a static and/or dynamical disorder in this crystals; the disorder is probably dynamical, i.e., ratchet (hopping) type rotation around the [111] direction; such a rotation is found below 450 K in fcc La@C_{82} crystals.[15] Further, the extremely large B [$=132(24)$ Å^2] in the model in which the Dy atom lies on the C_2 axis and the large B [$=25(7)$ Å^2] even when the Dy atom is displaced from the C_2 axis probably reflect the dynamical disorder of the Dy atom inside the C_{82} cage. In fact, a large floating motion of the La atom is found from the MEM electron density distribution of La@C_{82}.[25] The floating motion is also suggested from the theoretical electrostatic potential map.[26] Consequently, we have concluded that the Dy atom exhibits a large disorder, not only by the ratchet-type motion of the Dy@C_{82} molecule but also the floating motion inside the C_{82} cage; this disorder occurs around the [111] direction. The disordered molecules of Dy@C_{82} isomer I and a projection of the unit cell are shown in Figs. 5(a) and 5(b), respectively.

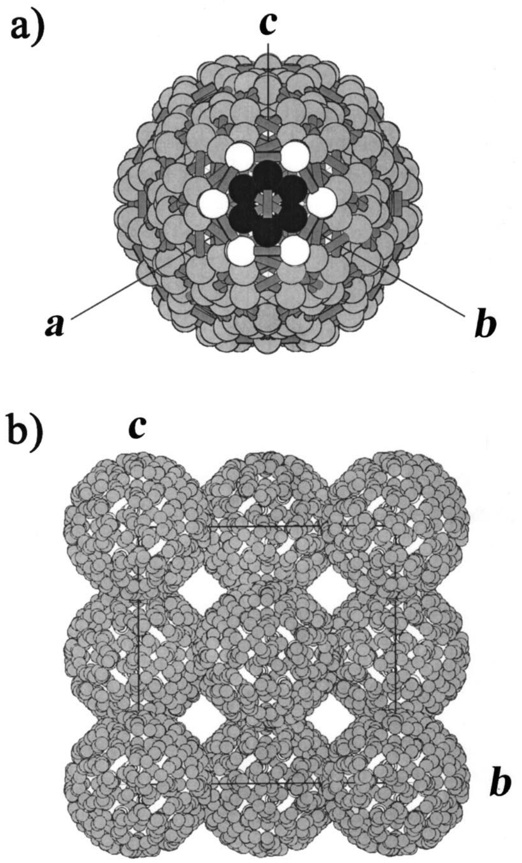

FIG. 5. (a) Structure of Dy@C_{82} molecules in the unit cell viewed along [111]. Six molecules are drawn to satisfy the $\bar{3}$ symmetry, and the cocupancies of the C and Dy atoms are 1/6. (b) Projection along [100] of the unit cell. In (a) the white and black circles refer to the C atoms in the six-membered ring and those in the fused six-membered rings, respectively; the C_2 axis of the cage passes through the six-membered ring and the center of the fused six-membered rings. The triple circles refer to the Dy atoms in (a) and (b).

The x-ray-diffraction pattern at 119 K was analyzed based on the space group $Pa\bar{3}$. The best fit is obtained for the cage-orientation of $\phi = 30°$ as in the case of 298 K: $R_{\mathrm{wp}} = 5.98\%$. a is 15.71(2) Å. The results show that the orientation of the C_{82} cage is constant at $\phi = 30°$ between 119 and 298 K. B of the Dy atom, 157(78) Å^2, was extremely large when the atom was placed on the C_2 axis of the cage. On the other hand, B was 16(7) Å^2 in a model in wich the Dy atom is displaced from the C_2 axis. In the analysis based on this model, the final R_{wp} and R_I were 5.86% and 6.13%, respectively. The position of the Dy atom at 119 K determined by Rietveld refinement is almost the same as that at 298 K. This

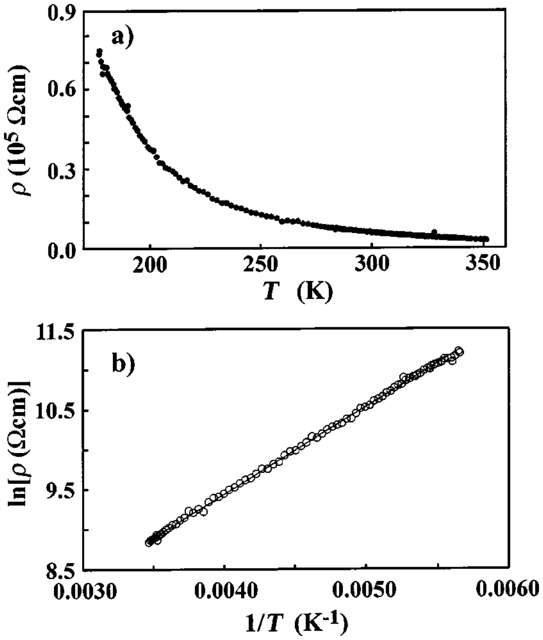

FIG. 6. (a) Plots of ρ vs T in a thin film of Dy@C_{82} from 170 to 350 K. Observed data are drawn by symbol ●. (b) Plots of $\ln\rho$ vs T from 170 to 290 K; the observed data are drawn by symbol ○. The solid line refers to that fitted with the linear relationship.

implies that the molecular structure of the Dy@C_{82} isomer I at 119 K is almost the same as that at 298 K, and the Dy atom exhibits large disorder.

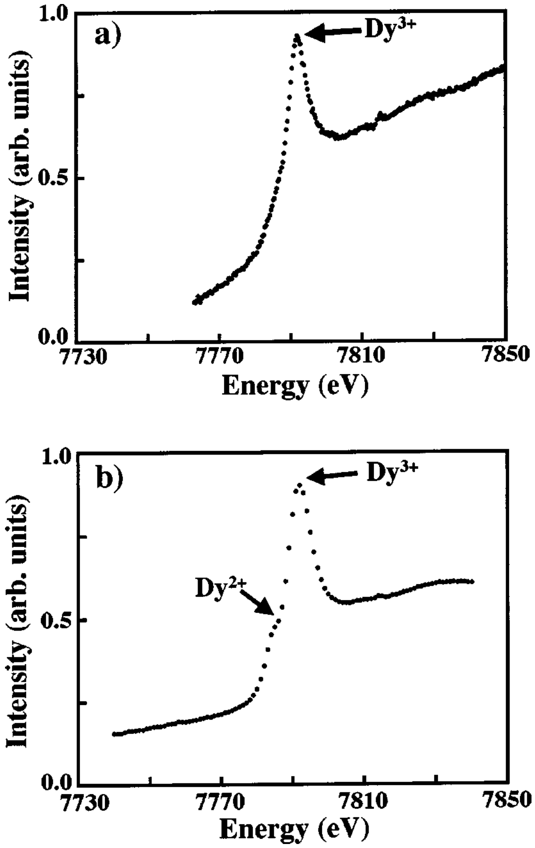

FIG. 7. XANES spectra of (a) Dy@C_{82} and (b) K_xDy@C_{82}.

Transport property of Dy@C_{82}

The temperature dependence of ρ of a thin film of Dy@C_{82} is shown in Fig. 6(a). The Dy@C_{82} sample used for the fabrication of thin film contains two isomers I and II, in which the abundance is estimated to be 4:1 from the integrated intensity of the HPLC peak.[9] ρ decreases with an increase in temperature up to 350 K. The ρ values are 6.8 kΩ cm at 290 K and 3.0 kΩ cm at 350 K. The $\ln\rho$ vs $1/T$ plots from 170 to 290 K are shown in Fig. 6(b), exhibiting a linear relationship. This implies that Dy@C_{82} is a normal semiconductor. E_g was estimated to be 0.2 eV which was smaller than those of C_{60} (1.8 or 2.1 eV), Na_4C_{60} (0.8 eV), K_4C_{60} (0.5 eV), Rb_4C_{60} (0.6 eV) and Cs_4C_{60} (0.6 eV).[27–30] The E_g value of Dy@C_{82} is slightly smaller than those of La@C_{82}, which are estimated to be 0.3 eV from the ρ for the single crystal[11] and 0.35 eV from the photoelectron spectroscopy.[12–14] These results show that Dy@C_{82} is a semiconductor with a small E_g. Such a small E_g suggests the possibility of the appearance of interesting physical properties in Dy@C_{82}. For example, the semiconductor-metal transition may be observed by applying pressure. No anomaly in the plots of ρ vs T was observed around 310 K. This implies that the structural phase transition of Dy@C_{82} isomer I has little effect on the transport property. Consequently, it can be concluded that the second-order phase transition observed around 310 K in Dy@C_{82} isomer I is the semiconductor-semiconductor transition.

Intercalation of K atoms into Dy@C_{82} crystals

The K metal was doped to the Dy@C_{82} crystals in order to prepare a new compound, K_xDy@C_{82}. The L_{III}-edge XANES spectra of Dy@C_{82} and K_xDy@C_{82} are shown in Figs. 7(a) and 7(b), respectively. The shoulder at 7785 eV is observed in addition to the peak at 7791 eV in K_xDy@C_{82}, while only the peak at 7791 eV was observed in Dy@C_{82}. The peak at 7791 eV for K_xDy@C_{82} can be associated with the Dy^{3+} because the peak for Dy@C_{82} is assigned to Dy^{3+}.[9] The shoulder may be assigned to the Dy^{2+} peak, from the analogy with the fact that the XANES peak (Eu^{2+}) in Eu@C_{60} shifts to lower energy by 6 eV in comparison with that (Eu^{3+}) in Eu_2O_3.[31] Thus the intercalation of K metal into the Dy@C_{82} crystals can result in the variation of valence from Dy^{3+} to Dy^{2+}. Recently, the sample of K_xTm@C_{82} was prepared, and its electronic structure was studied by photoemission spectroscopy.[32,33] In K_xTm@C_{82}, the existence of fcc structure of K_3Tm@C_{82} and bcc structure of K_6Tm@C_{82} is confirmed based on the relative intensity of C1s/K2p photoemission peaks. In this case, the valence of Tm (+2) did not change upon intercalation of K. This result is different from that in K_xDy@C_{82}. On the other

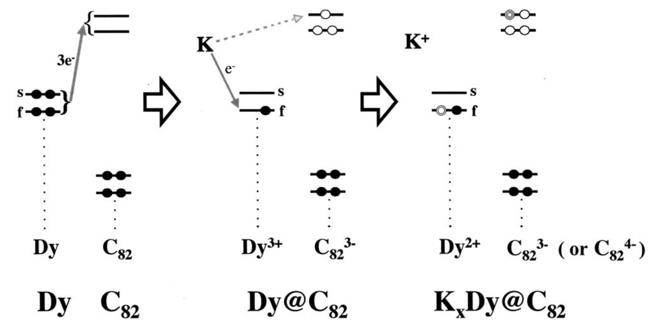

FIG. 8. Schematic representation of molecular orbitals of Dy@C_{82} and electron transfer between the metal atoms and C_{82}. Three electrons drawn by white circles refer to those transferred from the Dy atom to the C_{82} cage, while double and triple circles refer to the electrons transferred from the K atom. If the first electron from the K atom occupies the LUMO originated from the Dy atom, only a double circle is significant. On the other hand, the second electron drawn by the double circle occupies the LUMO originated from the Dy atom, if the first electron occupies the orbital originated from the C_{82} cage, as shown by the triple circle.

hand, the variation of valence of metal atom is found between metallofullerene and dimetallofullerenes from the UV-VIS absorption and XANES spectra.[34,35] The valences of Tm in Tm_2@C_{82} and TmHo@C_{82} are +3, while the valence of Tm in Tm@C_{82} is +2; the XANES peak of Tm@C_{82} shifts to the lower energy by 7 eV than that of Tm_2@C_{82}.[34]

We can propose the simple model that an electron released from K atom occupies the lowest unoccupied molecular orbital (LUMO) originated from the Dy atom in order to explain the variation of valence of Dy in K_xDy@C_{82}, as shown in Fig. 8. The LUMO originated from metal atom is theoretically suggested for Gd@C_{82},[26] The coexistence of Dy^{2+} and Dy^{3+} in this sample seems to imply the existence of K^+Dy^{2+}@C_{82}^3 and non-doped Dy^{3+}@C_{82}^{3-} rather than the solid-solution type phase with the mixed valence of Dy^{2+} and Dy^{3+}. This suggests that the *x* value of the K_xDy@C_{82} sample is less than 1.0. On the other hand, we can expect that the electron from the K atom occupies at first the orbital originated from the C_{82} cage, from the analogy with the electron transfer between the Dy atom and the C_{82} cage. In this case, after the electron-filling of the orbital of C_{82} cage, the electron must transfer to the LUMO originated from the Dy atom, in order to realize the valence of Dy^{2+} (Fig. 8). In this model, the valences of K, Dy, and C_{82} cages in KDy@C_{82} are +1, +3, and −4, respectively, and those in K_2Dy@C_{82} are +1, +2, and −4. This model is consistent with the fact that the charge on the C_{82} cage is −4 in La@C_{82}^-.[36]

The valence of the metal atom and the charge on the fullerene cage play an important role for physical properties of metallofullerenes. Many efforts have been directed so far to clarify the valence of the encapsulated metal atoms in metallofullerenes.[33,37] Recently, the interesting charge states such as M_3N^{6+} in M_3N@C_{80} and M_3N@C_{68} (*M*:Sc and/or Er), and Sc_3^{3+} in Sc_3@C_{82} are found.[38–40] Therefore, it is very interesting to study the valence of the encapsulated metal atoms in metal intercalated metallofullerenes. Krause *et al.* found a well defined relationship between the stretching mode of metal-cage and the valence of metal atom in metallofullerenes.[41] Consequently, a vibration spectroscopy such as Raman and IR as well as high energy spectroscopies such as XANES, x-ray photoemission, and X-ray absorption seem to be useful to confirm the valence-variation of Dy in K_xDy@C_{82}. A further investigation is necessary in order to obtain the conclusive evidence for the valence-variation of Dy in K_xDy@C_{82}, and to clarify its mechanism.

CONCLUSIONS

The crystal structure of the Dy@C_{82} isomer I has been determined by the Rietveld refinements for the X-ray-diffraction patterns at 298 and 119 K. It has been shown that the solvent-free crystals of the Dy@C_{82} isomer I take the space group of $Pa\overline{3}$ in the sc phase below 310 K. The C_2 axis of the C_{2v}-C_{82} cage in the Dy@C_{82} isomer I aligned along [111], and the Dy@C_{82} molecule is orientationally disordered around [111] to satisfy the $\overline{3}$ symmetry. The large *B* of the Dy atom estimated from the x-ray diffraction reflects the large disorder produced by both the ratchet-type rotation of the Dy@C_{82} molecule and the floating motion of the Dy atom inside the C_{82} cage. The crystal structure of the fcc phase of the Dy@C_{82} isomer I above 310 K is not discussed in the present paper. However, it can be expected that the sc structure changes to an fcc structure when the orientational disorder of the Dy@C_{82} molecule occurs with respect to all the axes of ⟨111⟩.

A semiconducting behavior is found for the Dy@C_{82} crystals from 170 to 350 K. E_g was estimated to be 0.2 eV. This shows that the Dy@C_{82} crystals are the small-gap semiconductors. Further, the intercalation of K atoms into the Dy@C_{82} crystals was tried, and the XANES spectrum was measured in order to determine the valence of the Dy atom. The valence of the Dy atom in Dy@C_{82} and Dy@C_{60} is reported to be +3 (Refs. 9 and 42); very recently, *M*@C_{60} compounds such as Dy@C_{60} were purified by the HPLC with aniline.[42–45] On the other hand, a peak was observed in K_xDy@C_{82} at an energy at 6 eV lower than that for Dy^{3+}. We assigned this peak to Dy^{2+}. If this is the case, the control of the electronic structure can be expected by metal doping into the metallofullerene solid.

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