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Study by X-ray diffraction and Raman spectroscopy of a $Dy@C_{82}$ single crystal

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Abstract. We report the first X-ray diffraction and Raman spectroscopy study of a single crystal of the rare-earth endohedral fullerene $Dy@C_{82}$. The lattice is found to be body-centered cubic ($a = 25.79$ Å, space group $I\bar{4}3d$) which is at variance with previous reports and confirms that several types of structures can be stabilized in $Dy@C_{82}$. X-ray diffraction/diffuse scattering methods reveal no low-temperature change down to 12 K for the present structure. The Raman spectroscopy data are comparable to those of other $M@C_{82}$ endohedral compounds. However, the Dy oxidation state and the force constant of the low-frequency metal-cage stretching mode do not follow the simple relationship observed before.

PACS. 61.10.Nz X-ray diffraction – 61.48.+c Fullerenes and fullerene-related materials – 78.30.Na Fullerenes and related materials

Introduction

The structures and electronic properties of metal endohedral fullerenes have attracted a large attention for the last years [1]. The number of studies have however been limited due to the low yield of endohedral metallofullerenes as compared with empty fullerene products. This limitation is even more severe for studies which require single crystals. We report here new results obtained on a $Dy@C_{82}$ single crystal by X-ray diffraction and Raman spectroscopy.

$M@C_{82}$ endohedral metallofullerenes have already been investigated in some details. Iida et al. [2] studied two isomers of $Dy@C_{82}$ with X-ray powder diffraction, XAFS and UV-VIS absorption. Takabayashi et al. [3] measured the lattice constant of $Dy@C_{82}$ with X-ray powder diffraction at pressures up to 60 kbar. Several other $M@C_{82}$ compounds (M = Y, La, Ce, and Gd) have been studied by Raman spectroscopy, and Lebedkin et al. [4] proposed a model for the low-frequency metal-to-cage vibration modes observable in the Raman spectrum. Krause et al. [5,6] performed similar studies on a broader range of endohedral metallofullerenes, including the above-mentioned $M@C_{82}$ compounds plus $Sm@C_{82}$ and $Tm@C_{82}$.

C_{82} can theoretically form nine different isomers, still obeying the pentagon isolation rule. But an NMR study reported that only three isomers, all having C_2 symmetry, could be found [7]. When doping the C_{82} cage endohedrally with Dysprosium, Iida et al. [2] managed to separate two different isomers, with symmetries C_{2v} and C_s, and with relative abundance 4:1. A Rietveld analysis of the $La@C_{82}$ powder diffraction also revealed a C_{2v} symmetry for the C_{82}-cage [8].

One of the questions regarding the $M@C_{82}$ compounds concerns the charge transfer from the encapsulated atom to the C_{82} cage. A recent study by XANES has shown that the Dy atom donates three electrons to the carbon cage [2], in the same way as Y [9,10], Gd [11], La [9,11–13], and Ce [14]. Furthermore, analyses of the metal-cage vibration modes observed in the Raman spectra were used to confirm the +3 oxidation state for Y, La , Ce, and Gd, while Sm and Tm were assigned +2 [4,5]. It is thus interesting to compare our Raman results on $Dy@C_{82}$ with these previous reports.

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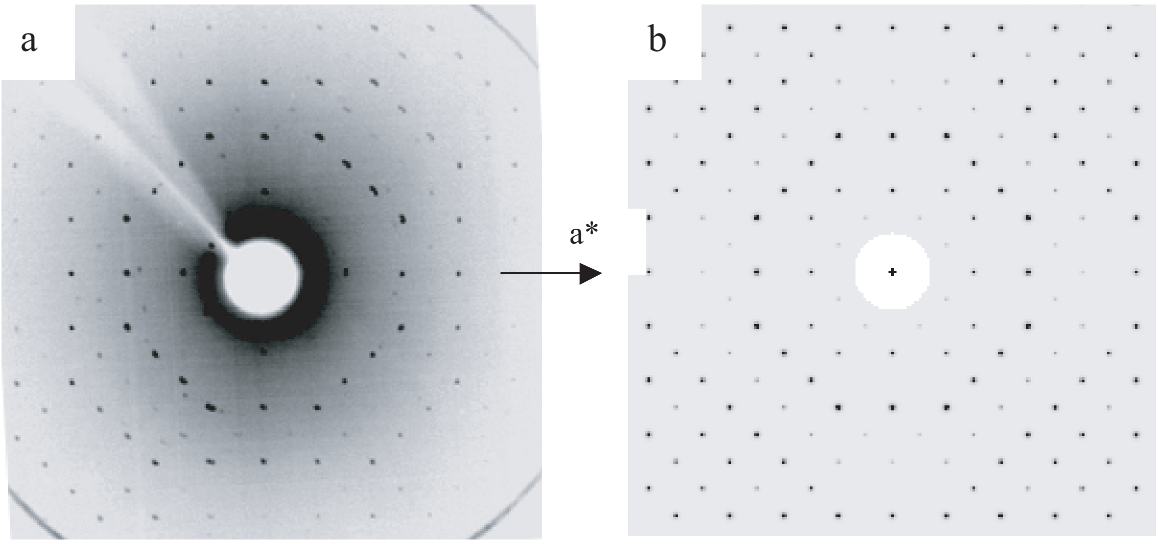

Fig. 1. (a) Diffraction pattern (CuKα precession photograph) of the Dy@C$_{82}$ crystal for the reciprocal layer ($hk1$). (b) Calculated pattern using a model structure similar to that of La@C$_{82}$(CS$_2$)$_{1.5}$.

Experimental details

The soot produced by the arc-discharge method was collected and a Dy@C$_{82}$ solution was isolated by high performance liquid chromatography (HPLC). Single crystals were grown using the solvent diffusion method by letting acetone diffuse into the toluene solution. After several weeks, the crystals grew due to the different solubilities in the two solvents. The present crystal has a prismatic shape (about 85 μm in length and 50 μm in width). It was handled in air and mounted on a thin copper wire by a small drop of GE varnish. Room-temperature precession and low-temperature stationary photographs were collected using monochromated CuKα radiation (a doubly-bent (002) HOPG graphite monochromator was used). The low-temperature experiments were performed using the fixed-crystal technique. Both X-ray films and imaging plates were used.

The Raman studies were performed using a Renishaw 1000 grating spectrometer with a notch filter to remove the Rayleigh line and a Peltier cooled CCD-detector. As probing laser we used a He-Ne (632.8 nm) laser focused to a 5 μm spot. The power density on the sample was less than 10 W/cm^2.

Results and discussion

X-ray diffraction

A comprehensive set of precession patterns for various reciprocal planes was recorded to derive the unit cell and space group of our Dy@C$_{82}$ crystal. These data clearly show that the lattice has a cubic symmetry and the cell parameter is found to be $a = 25.79$ Å. Figure 1a shows a typical precession pattern for the $l = 1$ reciprocal plane. This pattern together with all diffraction data match the $(h + k + l = 2n)$ reflection condition for a body-centered Bravais lattice. Moreover the general reflection conditions $0kl$: $k + l = 2n$; hhl: $2h + l = 2n$ and $h00$: $h = 4n$ are fulfilled, which uniquely characterizes the $I\bar{4}3d$ space group.

It is worth comparing our structural results with those earlier obtained on Dy@C$_{82}$ and also on La@C$_{82}$, which has been the most studied metallofullerene (most studies used powder samples but a few were made on single crystals like the present one). For La@C$_{82}$ two different structures have been reported. Suematsu et al. [15] performed both X-ray powder diffraction and precession photographs on tiny single crystals of La@C$_{82}$(CS$_2$)$_{1.5}$. They could characterize the structure as body-centered cubic (bcc, space group $I\bar{4}3d$). On the other hand, La@C$_{82}$ containing toluene has been shown to form a P2$_1$ monoclinic structure by Nishibori et al. [8], while Watanuki et al. [16], reported a face-centered cubic (fcc) structure ($a = 15.78$ Å) at room temperature for a presumably solvent-free La@C$_{82}$ single crystal. Concerning Dy@C$_{82}$, also considered as solvent-free, Iida et al. [2] and Takabayashi et al. [3] found by X-ray powder diffraction that the isomer with C_s symmetry adopts a fcc structure while the C_{2v}-symmetry isomer adopts a simple cubic (sc) structure ($a = 15.79$ Å). However, the latter transforms into an fcc structure above 300–310 K [3].

In the present study we have not attempted to select and isolate a specific isomer and we have not determined which isomer is present in our crystal. However, given that the C_{2v} isomer was found to be more abundant (C_{2v}/C_s is in a 4/1 ratio) [2] we can estimate that our crystal contains primarily C_{2v} or a mixture of both isomers. In any case, the unit cell and space group we have found for the present crystal do not agree with the above results for Dy@C$_{82}$. Instead they correspond very well to those

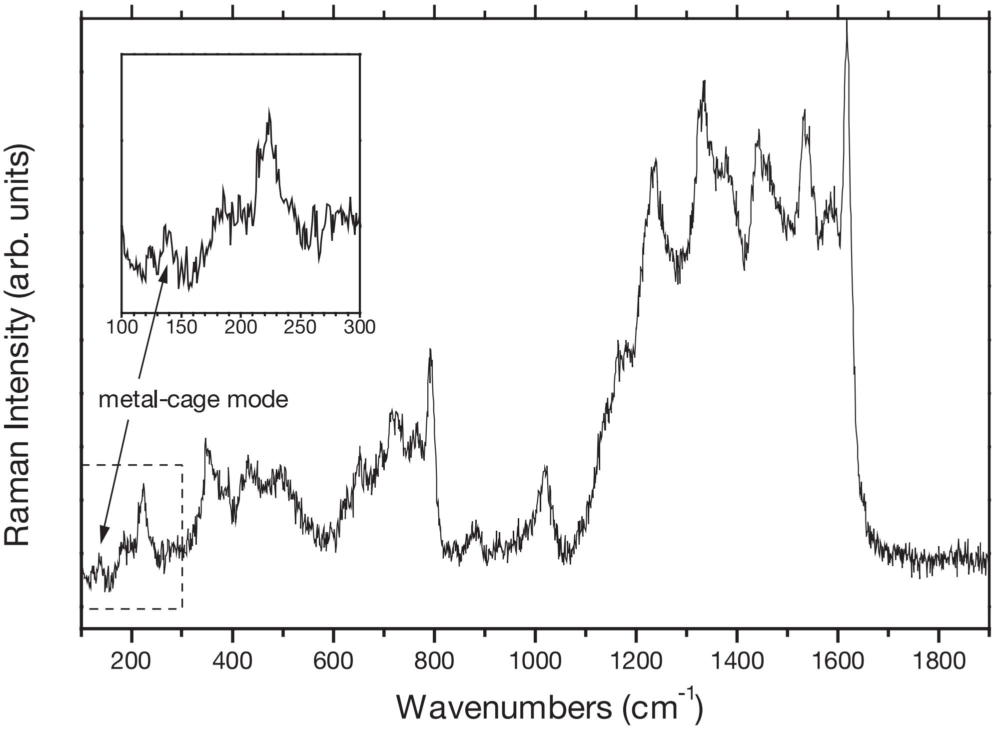

Fig. 2. Raman spectra of Dy@C_{82}, obtained with a He-Ne laser (632 nm). The inset shows the low-frequency region with the peak attributed to the metal-cage stretching mode.

obtained by Suematsu et al. [15] for La@$C_{82}(CS_2)_{1.5}$, containing about 1.5 carbon disulfide molecules per La@C_{82} (the unit cell parameters are close: $a = 25.79$ Å (Dy@C_{82}) as compared to $a = 25.72$ Å (La@C82)). This is unexpected because (i) our Dy@C_{82} crystals was grown with a toluene/acetone mixture but no carbon disulfide (CS_2) was used, (ii) toluene solvates appear to crystallize with a monoclinic symmetry (this is the case for the La metallofullerene), (iii) Raman spectroscopy data do not reveal any traces of toluene, e.g three relatively distinct peaks around 1200 cm^{-1}, in our sample (see Fig. 2). Neither do any traces of acetone show up in the Raman spectrum, e.g a large mode at 1713 cm^{-1}. At the moment we have no satisfactory explanation for these results which add to the already complex range of distinct structures exhibited by the endohedral metallofullerenes.

To test whether the crystal structure determined by Suematsu et al. [15] for La@$C_{82}(CS_2)_{1.5}$ could be used as a first-step model for the structure of our Dy@C_{82} crystal we have simulated our X-ray diffraction patterns as follows. We have calculated the Bragg reflection intensities using the following assumptions: (i) Dy and C_{82} occupy the same positions as La and C_{82} (i.e. with shifts of 1.78 Å (La) and 1.11 Å (C_{82}) along ⟨111⟩, in opposite directions), (ii) the C_{82} molecule is approximated as a spherical shell with radius 4.1 Å (to take into account the possible mixture of the C_{82} isomers and their disorder, both orientational and occupational), (iii) there is no solvent in the unit cell. As an example Figure 1b shows the $(hk1)$ diffraction pattern calculated with this model structure. Comparison with Figure 1a reveals that the observed and simulated intensity distributions present common features indicating that, in a first approximation, the arrangement of the rare earth cations and C_{82} molecules may be similar in Dy@C_{82} and La@$C_{82}(CS_2)_{1.5}$. However, the disorder of the C_{82} molecule is certainly more complex than that described by a spherical shell model. It may be similar to the case of Y@C_{82} [17] or La@C_{82} [8] , for instance, where Rietveld and Maximum-Entropy Methods (MEM) have found that the electronic density on the C_{82} cage is not homogeneous and exhibits local maxima. The orientational disorder produces X-ray diffuse scattering which could be measured and analyzed to provide information on the nature and strength of the intermolecular interactions, as was done for pristine C_{60} [18]. However, we have not been able to detect any disorder-type diffuse scattering intensity from our crystal, presumably because of its small size. Further attempts should be made when larger crystals become available.

We also performed low-temperature X-ray diffraction experiments using the fixedcrystal method. No evidence for a phase transition was found in the 300–12 K temperature range. This is at variance with the observation, using a similar X-ray technique, of phase transitions attributed to orientational ordering in solvent-free La@C_{82} [16].

Table 1. Raman modes for Dy@C_{82} between 100 and 2000 cm^{-1}, comparison is made with the modes listed for M@C_{82} (M = Y, La, Gd and Ce), from Lebedkin et al. [4], (only listed between 100–800 cm^{-1}).

Dy@C_{82} (cm^{-1})	Y@C_{82} [4]	La@C_{82} [4]	Gd@C_{82} [4]	Ce@C_{82} [4]
140	183	163	155	162
224	223	215	215	217
		250	230	246
356	360	362	361	362
432	434	431	432	
	566		565	
654	630	630	628	634
695	694	692	694	695
726	733	733	732	731
767	770	767	768	770
793	794	795	794	795
882				
1020				
1175				
1236				
1331				
1376				
1443				
1538				
1587				
1615				

Raman spectroscopy

Turning our attention to the Raman spectrum presented in Figure 2 and in Table 1 we notice a striking resemblance with the previously reported Raman spectra of other M@C_{82} compounds [4,5].

The rather complex Raman spectra of M@C_{82} makes it relatively hard to assign the different peaks to specific vibrational modes. However, nearly all medium and high-frequency (above 200 cm^{-1}) peaks match, irrespective of the nature of the endohedral metal (see Tab. 1, compare Fig. 2 with Fig. 2 in Ref. [4]). This implies that the modes correspond to carbon-carbon vibrations on the C_{82} molecule and that these are more or less unaffected by the type of metal inserted. This is in agreement with the previous Raman studies [4,5].

Concerning now the low-frequency peaks observed below 200 cm^{-1}, Lebedkin et al. [4] attributed these modes to the metal atom-carbon cage stretching vibrations and suggested that they could be approximated using a simple harmonic oscillator model, with a frequency given by

$$\nu\ (\mathrm{cm}^{-1}) = 1302.1(f/\mu)^{1/2}.$$

where f is the force constant ($\mathrm{N\,cm^{-1}}$) and μ is the reduced mass (atomic mass units) of the M-C_{82} system. A similar approach was adopted by Krause et al. [5].

The present spectrum exhibits a low-frequency peak at 140 cm^{-1} (Fig. 2, inset) that can also be ascribed to a metal atom-carbon cage mode, i.e. Dy-C_{82} stretching vibrations. In Table 2 we add this mode to the data taken from references [4] and [5]. Note that a smaller peak, at about 125 cm^{-1}, is also visible; it is not considered below as its origin is unclear (possibly an isomer effect or some disorder associated with a different state of the metal atom-carbon cage bonding).

The force constants derived using the above equation for the M@C_{82} compounds (with M= Y, La, Ce, Gd, Dy, Sm and Tm) are given in Table 2 (incidentally we mention that in Ref. [4] the linear fit shown in Fig. 3 does not correspond to the force constant as the straight line does not go through the origin of the graph). The force constants are linked to the nature and strength of the metal-cage bonding, which should depend on the oxidation state of the inserted metal. Using such type of reasoning Krause et al. [5] separated the rare-earth M@C_{82} into two groups: the oxidation state +3 was proposed for La, Ce and Gd whose force constants are about 1.91 $\mathrm{N\,cm^{-1}}$ while +2 was ascribed to Sm and Tm which have significantly softer force constants (about 1.2 $\mathrm{N\,cm^{-1}}$). It appears that Dy@C_{82}exhibits a singular behavior because the rare-earth Dy atom has been shown to give 3 electrons to C_{82} [2] while the present result indicates a weaker bonding than for the other rare-earth $M^{3+}C_{82}^{3-}$ compounds. The force constant for Dy@C_{82} is actually intermediate between those of the +3 and +2 groups mentioned above and it is the same as for $Y^{3+}C_{82}^{3-}$ (but Y is not a rare-earth metal). These results suggest that more complex mechanisms play a role and more elaborate models should be considered in order to understand the metal-fullerene bonding in these endohedral compounds.

In summary, we have shown that a Dy@C_{82} single crystal crystallizes in a bcc structure with lattice parameter a = 25.79 Å, and space group $I\bar{4}3d$. This unit cell and space group are similar to those of La@$C_{82}(CS_2)_{1.5}$ structure, which is not understood as our crystal was grown out of a toluene/acetone mixture (no carbon disulfide was used) and, moreover, the presence of toluene and acetone in significant amount is ruled out by Raman spectroscopy. The nature of the various structures found for the M@C_{82} metal endohedral compounds and their solvates still need to be clarified.

The Raman spectrum of Dy@C_{82} displays the same general trends as other M@C_{82} compounds. However it

Table 2. Reduced masses, metal-cage vibrations and force constants of M@C_{82} endohedral fullerenes.

	Reduced mass (μ) (atomic mass units)	Metal to cage vibration (cm^{-1})	Force constant ($N\,cm^{-1}$)
Y@C_{82}	81.54	183 [4], 177 [5]	1.61 [4], 1.50 [5]
La@C_{82}	121.74	163 [4], 162 [5]	1.91 [4], 1.88 [5]
Ce@C_{82}	122.67	162 [4], 156 [5]	1.90 [4], 1.76 [5]
Gd@C_{82}	135.61	155 [4], 152 [5]	1.92 [4], 1.85 [5]
Dy@C_{82}	139.49	140	1.61
Sm@C_{82}	130.44	125.5 [5]	1.21 [5]
Tm@C_{82}	144.20	118 [5]	1.18 [5]

does not obey the simple relationship established previously [5] between the oxidation state of the rare-earth metal atom and the force constant of the low-frequency metal-cage stretching modes.

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