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Monometallofullerene Tm@C_{82}: Proof of an Encapsulated Divalent Tm Ion by High-Energy Spectroscopy

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The valency of the Tm ion in the endohedral monometallofullerene Tm@C_{82} with C_{3v} symmetry has been studied using high-energy spectroscopy. The resemblance of the Tm 4d core level photoemission spectrum to that calculated for Yb^{3+} suggests a $4f^{13}$ ground state configuration for the encapsulated Tm ion. This could be proven beyond doubt by measurements of the characteristic 4f multiplet structure in photoemission. Furthermore, the Tm 4d excitation spectrum measured using volume sensitive electron energy-loss measurements in transmission confirms that this material is indeed the first monometallofullerene containing a divalent lanthanide ion. [S0031-9007(97)04301-9]

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The ability of fullerene molecules to encapsulate one or more metal ions inside their carbon cage has captured the imagination of many researchers. These so-called metallofullerenes represent a truly novel type of matter, which is expected to display remarkable electronic and structural properties in comparison to the empty fullerene cages [1]. After the first observation of metallofullerenes in 1985 [2], several different endohedral fullerenes have been purified and isolated in macroscopic quantities. In the past, much work has been carried out on metallofullerenes of La [3,4], Y [5], and Sc [6], whereby C_{82} and C_{84} form the host cages. More recently, metallofullerenes containing rare earth ions have been produced, such as Gd [7] and Tm [8].

Until the present, the charge distribution in monometallofullerenes has been discussed exclusively in terms of M^{3+}@C_{82}^{3-} in agreement with the observation of a signal in electron spin resonance experiments [4–6]. This view is also consistent with theoretical predictions [9] and with the analysis of the electron density distribution of a Y@C_{82} microcrystal as measured by x-ray diffraction [10]. Very few direct studies of the valency of the various endohedral metal ions have been reported. X-ray photoemission spectroscopy (XPS) has been shown to be a suitable probe of the valency of the La in La@C_{82} [5,11]. In this case, the comparison of the La 3d core level spectrum with those of various La trihalides showed that the La is trivalent, with the $(C_{82})^{3-}$ providing an environment slightly less electronegative than that in $LaBr_3$ [11]. In the case of the lanthanide monometallofullerene Tm@C_{82}, a series of physical and chemical studies in solution of the three different isomers has been found to be consistent with a Tm^{2+}@C_{82}^{2-} charge distribution [8], but the Tm valency could not be unambiguously determined.

In this contribution we present a detailed investigation of the valency of Tm in the endohedral monometallofullerene isomer of Tm@C_{82} with C_{3v} symmetry using high-energy spectroscopy. We present conclusive proof of the divalent nature of the single encaged Tm ion in this material, making this the first divalent lanthanide monometallofullerene.

The preparation and separation of the three different isomers of Tm@C_{82} has been described previously [8]. After purification by multicycle chromatography, recrystallization from CS_2 and degassing in ultrahigh vacuum (UHV) at 160 °C for 48 h, thin films of the C_{3v} isomer of Tm@C_{82} were prepared for photoemission by sublimation onto freshly evaporated copper films in UHV at 780 °C. The samples were then transferred under UHV conditions into the spectrometer where they were studied using monochromatic Al K_α radiation (1486.6 eV) with an energy resolution of 350 meV. The spectra of the Tm@C_{82} contained no contribution from the substrate, remaining solvent, or any other contaminations. All photoemission lines could be attributed to either Tm or C. For the electron energy-loss spectroscopy (EELS) experiments, thin films of about 1000 Å thickness were sublimed onto KBr single crystals in UHV. After subsequent dissolution of the crystal, the samples were mounted on standard electron microscope grids and transferred into the spectrometer, which is described elsewhere [12]. The Tm 4d excitation edges were measured with an overall energy resolution of 160 meV.

The first source of information regarding the Tm valency is the Tm 4d core level photoemission spectrum as shown for Tm metal and the C_{3v} isomer of Tm@C_{82} in Fig. 1. A simple analysis of the binding energy (BE) position of the Tm 4d main line in terms of the charge state of the Tm ion is complicated by the strong interaction between the holes in the 4d and 4f shells in the photoemission final state [13]. This leads to a broad multiplet structure with intensity distributed over a range of more than 30 eV. Nevertheless, the position of the Tm 4d main line in the metallofullerene is shifted by about 2.5 eV to lower BE in comparison to that in trivalent Tm metal (175.2 eV BE), which suggests a Tm valency lower than three in the endohedral fullerene. As there appear to be

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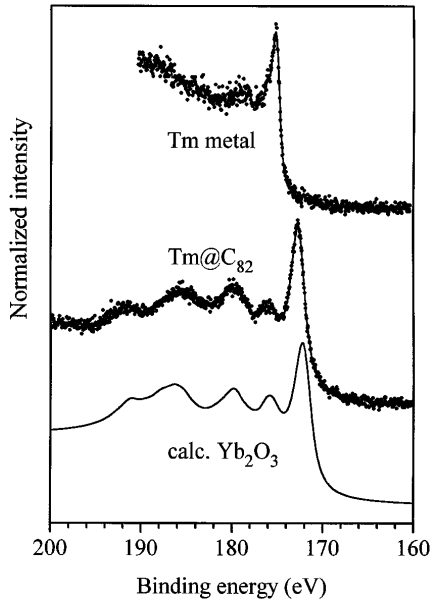

FIG. 1. XPS spectra of the Tm 4d core level of Tm metal (upper spectrum) and the C_{3v} isomer of Tm@C_{82} (lower spectrum) as well as calculated 4d XPS spectrum of Yb^{3+} from Ref. [13] (solid line).

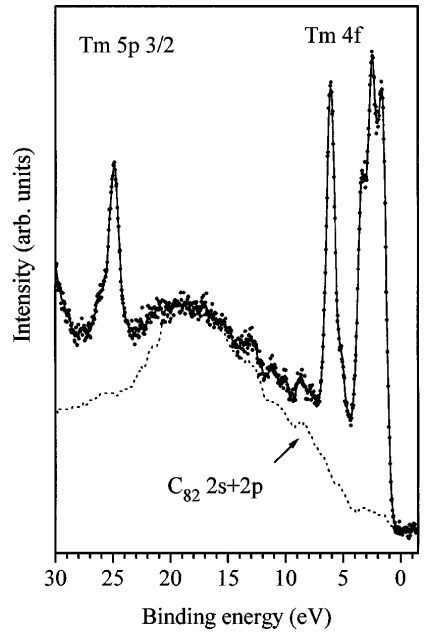

FIG. 2. Valence band XPS spectrum of the C_{3v} isomer of Tm@C_{82}. The dotted line is the spectrum of empty C_{82} from Ref. [11].

no 4d photoemission spectra of divalent Tm compounds in the literature, we compare our results to the calculated spectrum for trivalent Yb from Ref. [13] (shown as a solid line in Fig. 1), which has also a $4f^{13}$ ground state configuration. Although matters are further complicated in such rare earth 4d photoemission by the lifetime-dependent intensity of the different multiplet lines [13], it can be seen that the good agreement provides the first evidence for a $4f^{13}$ ground state in the Tm monometallofullerene [14]. Measurement of the Tm 4d core level does allow, however, the confirmation of the endohedral nature of the Tm ion, as air exposure showed no effect on either the position or the shape of the Tm 4d profile in Tm@C_{82}.

A quantitative probe of the valency of rare earth systems is offered by measurements of the characteristic multiplet structures in 4f photoemission. Therefore, we have studied the valence band photoemission of the monometallofullerene in detail. For Al K_α radiation, the relative photoionization cross sections of the 4f states are strongly enhanced compared to those of C 2s and 2p. Therefore the XPS valence band spectrum is dominated by the Tm 4f multiplets [15], as can be seen in Fig. 2 . Here, the Tm 5p and 4f multiplets can be easily identified upon comparison with the spectrum of C_{82} from Ref. [11], which is shown as a dotted line. Upon subtraction of the C 2s and 2p background, we obtain the spectral signature of the Tm 4f multiplets alone, which is shown in detail in the lower part of Fig. 3. Also plotted in Fig. 3 is the 4f spectrum of trivalent Tm metal, as well as the calculated multiplet profiles for $4f^{12} \rightarrow 4f^{11}$ and $4f^{13} \rightarrow 4f^{12}$ photoemission [16,17].

These characteristic 4f multiplet structures have been widely studied [16,18] and can be used as a fingerprint for the charge state of the rare earth atom in question. For example, both trivalent Tm metal [19] and divalent Tm in TmTe [20] have been studied in this manner. For Tm compounds of mixed trivalent/divalent character

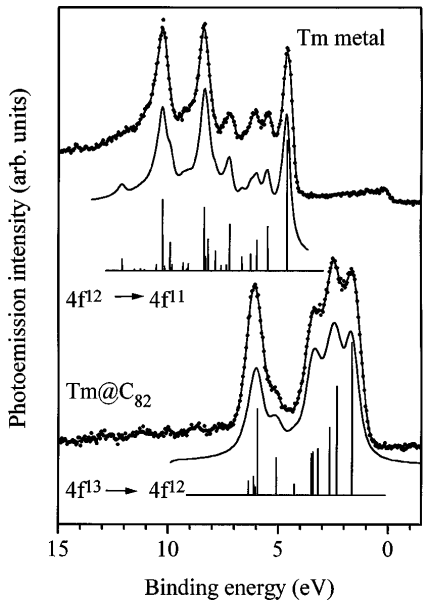

FIG. 3. 4f photoemission spectra of Tm metal and the C_{3v} isomer of Tm@C_{82} (the C_{82} background has been subtracted). Below each spectrum the calculated multiplet distribution for $4f^{12} \rightarrow 4f^{11}$ and $4f^{13} \rightarrow 4f^{12}$ photoemission after Ref. [16].

such as TmSe a superposition of the $4f^{12}$ and the $4f^{13}$ configuration has been used to extract an average valency of the material under investigation [21,22].

The excellent agreement between the $4f$ multiplets of the C_{3v} isomer of Tm@C_{82} and the calculated multiplet spectrum for $4f^{13} \rightarrow 4f^{12}$ photoemission clearly indicates a charge transfer of only *two* electrons to the carbon cage, thus giving a Tm^{2+} charge state. Moreover, no contribution from trivalent Tm is detected, showing that the weight of the $4f^{12}$ configuration in the ground state is vanishingly small. This is in contrast to the case of Tm metal (shown in the upper part of Fig. 3) or other trivalent or mixed valent Tm systems where an unambiguous contribution from a $4f^{12}$ ground state is observed. The formal $Tm^{2+}@C_{82}^{2-}$ charge distribution in this system is in stark contrast to all other lanthanide monometallofullerenes, and indicates the complex interplay between the metal ionization potential and the low lying unoccupied electronic states of the fullerene isomer in question. This point underlines the importance of using isomer-separated fullerenes for high-energy spectroscopic investigations as the influence of isomerization on the electronic levels of empty fullerenes has been found to be surprisingly large [23].

In many photoemission investigations of rare earth valency, care has to be taken to account for the reduced valence of the rare earth atoms in the surface layers [24]. However, this should not present such a problem in Tm monometallofullerene, as such endohedral fullerenes can be considered as paradigm surfaceless rare earth systems, as was alluded to above in the discussion of air-stability. Nevertheless, further evidence for divalent Tm is given by the bulk sensitive measurement of the Tm $4d$ excitation spectrum of the monometallofullerene using EELS in transmission, which is shown in the lower part of Fig. 4. In Fig. 4 we also include soft x-ray absorption measurements of Tm metal recorded using the total electron yield mode from Ref. [25] (upper part).

From the selection rules within the Russel-Saunders coupling scheme, the allowed absorptions for the $4f^{12}$ and $4f^{13}$ initial state configurations give $4d^9 4f^{13}$ final states with $3H_6$, $3H_5$, and $3G_5$ symmetry and a $4d^9 4f^{14}$ final state with $2D_{5/2}$ symmetry, respectively [26]. These final states match the experimental spectra for Tm metal and the monometallofullerene nicely. Thus, the Tm $4d$ excitation spectrum of the endohedral shown in Fig. 4 quite clearly indicates a $4f^{13}$ ground state, with no indication of trivalent Tm.

In conclusion, we have presented a detailed study of the valence of Tm encapsulated in the C_{3v} isomer of Tm@C_{82}. The multiplet structures in both the $4d$ and $4f$ photoemission as well as the $4d$ excitation spectrum prove unambiguously the pure $4f^{13}$ ground state configuration of the Tm ion in the monometallofullerene. Therefore Tm@C_{82} represents the first divalent rare earth endohedral monometallofullerene. Compared to the

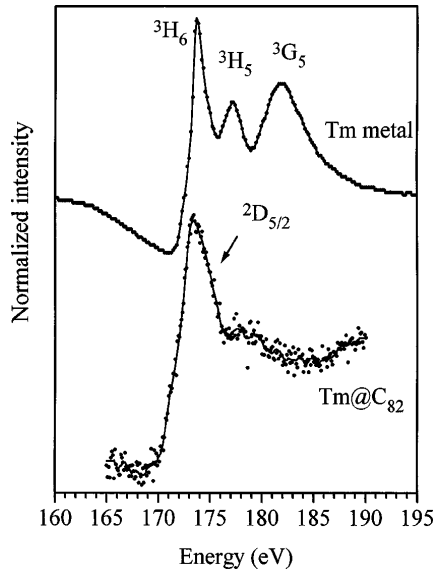

FIG. 4. Below: Tm $4d$ excitation spectrum of the C_{3v} isomer of Tm@C_{82} measured using EELS in transmission. Above: The corresponding spectrum of Tm metal from Ref. [25].

other monometallofullerenes M@C_{82} (M = La, Y, Sc) where the metal ion is off center as found by x-ray diffraction [10] and predicted by *ab initio* calculations [9,11], Tm@C_{82} may be the first example, where the rare earth ion is more in the central position, since the divalent rare earth ions have a larger size compared to trivalent rare earth ions.

In general, the described high-energy spectroscopic methods supply a direct proof of the valency of all other lanthanide ions with partially filled $4f$ shell encapsulated in fullerene cages. Especially in the case of rare earth ions with well known mixed valent and/or divalent compounds like Sm, Eu, and Yb these methods are an ideal probe to measure the effective average valency of their metallofullerenes.

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