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Proof for trivalent Sc ions in $Sc_2@C_{84}$ from high-energy spectroscopy

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The electronic structure and the valency of the Sc ions in the endohedral dimetallofullerene $Sc_2@C_{84}$ with D_{2d} symmetry are probed using high-energy spectroscopy. Comparison of the Sc $2p\rightarrow 3d$ x-ray-absorption spectrum with calculated ionic multiplet spectra shows that the Sc ions are trivalent. Detailed multiplet calculations including covalency indicate that the effective valency of the Sc(III) ions can be described by a formal charge transfer to the fullerene cage of 2.6 ± 0.1. This illustrates that a purely ionic picture is not valid for the electronic structure of $Sc_2@C_{84}$, and that a more complex picture including finite hybridization between the Sc and the fullerene cage has to be applied.

I. INTRODUCTION

The ability of fullerene molcules to encapsulate one or more metal ions inside their carbon cage has captured the imagination of many researchers. These so-called metallofullerenes represent an interesting 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 were 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,[6,7] in which C_{82} and C_{84} form the host cages. Among the dimetallofullerenes, $Sc_2@C_{84}$ received the most attention so far. After the first production[8] and isolation of $Sc_2@C_{84}$ by high-pressure liquid chromatography, three different structural isomers were identified by ^{13}C NMR.[9] From scanning tunneling microscopy[10] and transmission electron microscopy[11] the endohedral nature of the metallofullerenes was suggested. Recent x-ray-diffraction experiments confirmed the endohedral nature of this dimetallofullerene.[12] In addition, experiments measuring the spectroscopic and vibronic properties,[8,13,14] as well as first measurements of the electronic structure using photoemission, were performed.[15]

From quantum-chemical calculations the encaged transition-metal ions in these dimetallofullerenes were predicted to be divalent.[16,17] This prediction appeared to be borne out by an analysis of the electron-density distribution of a $Sc_2@C_{84}$ microcrystal as measured by x-ray diffraction, which suggested a charge density at the Sc atom of $+2.2$.[12] In recent Raman measurements analyzing the valence force constant Sc-C_{84} within a simple linear three mass oscillator model,[14] a charge transfer of slightly more than two electrons per Sc ion to the carbon cage was also suggested.

However none of these methods is a direct probe of the valency of the encaged ions and the effective charge distribution within the cage. Therefore, the results from these measurements have to be regarded with some caution. Photoemission spectroscopy and x-ray-absorption spectroscopy (XAS) were shown in the past to be well-suited site-selective probes for the valency of transition-metal ions and rare-earth ions.[18,19] In the case of the endofullerenes, x-ray photoemission spectroscopy (XPS) was shown to be an ideal probe of the valency of encaged rare-earth ions in metallofullerenes. For $La@C_{82}$ the comparison of the La $3d$ core-level spectrum with those of various La trihalides showed that La is trivalent, with $(C_{82})^{3-}$ providing an environment slightly less electronegative than that in $LaBr_3$.[20] Further experiments using resonant photoemission at the La $3d$ threshold clearly showed a resonant enhancement of features in the valence band corresponding to La $5d$ states, thus pointing out the existence of finite hybridization between La $5d$- and

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$2p$-derived states from the carbon cage.[21] In the case of lanthanide metallofullerenes the characteristic $4f$ multiplets of the rare-earth ion and the $4d \rightarrow 4f$ absorption edges were used as a fingerprint of the valency. For $Tm@C_{82}$ an unusual valency of two was observed, which is independent of the symmetry of the host carbon cage.[22,23]

Much less has been reported as regards the transition-metal metallofullerenes. For $Sc_2@C_{84}$, only initial XPS experiments of the Sc $2p$ lines on air-exposed samples of films of the isomer with D_{2d} symmetry were carried out, and these were interpreted in terms of divalent Sc ions.[15] However, the analysis of the chemical shift of the Sc $2p$ line alone allows no determination of the effective charge distribution in this dimetallofullerene, pointing out the need for further, more conclusive experiments.

In this paper we present a detailed investigation of the valency of the Sc ions in the endohedral dimetallofullerene $Sc_2@C_{84}$ using photoemission spectroscopy and x-ray-absorption spectroscopy. We present conclusive proof for trivalent Sc(III) ions encaged in C_{84}, which is in contrast to theoretical predictions and to estimations of the valency from earlier, indirect experiments on this material.

II. EXPERIMENTAL AND THEORETICAL BACKGROUND

The preparation and separation of the three different isomers of $Sc_2@C_{84}$ was described previously.[8] After purification by multicycle chromatography,[9] the $Sc_2@C_{84}$ was put into an alumina crucible and degassed in an effusion cell in ultrahigh vacuum at 160 °C for 48 h, and at 400 °C for 30 min. For the photoemission and x-ray-absorption experiments, thin films of a thickness of about 200 Å of the D_{2d} isomer of $Sc_2@C_{84}$ were prepared by sublimation onto freshly evaporated gold films in UHV at 680 °C. The samples were then transferred under UHV conditions into analysis chambers equipped with commercial hemispherical electron analyzers, and a total electron yield detector, respectively. Ultraviolet photoemission [using monochromatized He I radiation (21.2 eV)] and x-ray photoemission [using monochromatic Al K_α radiation (1486.6 eV)] were carried out with energy resolutions of 20 and 350 meV, respectively. The Sc $2p$ excitation edges and photoemission at different photon energies were measured at the high-resolution undulator beamline U125/PGM at BESSY II with an overall resolution at 400 eV of 100 meV. The photon energy was calibrated using the Au 4 $f_{7/2}$ peak of the clean substrate.

Calculations of the Sc $2p$ XAS lines were performed using the multiplet approach. Both the crystal-field multiplet (CFM) model and the charge-transfer (CT) model were used. The CFM model is a single configuration calculation for Sc ions. The atomic interactions are included for a Sc^{n+}, ion and the chemical surroundings are calculated using an electrostatic crystal field. This method has been used for Sc^{3+} ions with a $3d^0$ configuration simulating Sc_2O_3 and ScF_3.[18] For a $3d^1$ configuration Ti^{3+} ions which are isoelectronic to Sc^{2+} were calculated.[19] The CT model extends the CFM model by using multiple configurations, for example $3d^0 + 3d^1\underline{L}$, where $\underline{L}$ stands for an electron transfer from the surroundings to the central atom.[24] The simplest way to arrive at the effective $3d$ count is by mixing two configurations in the calculations. This approach will be used here.

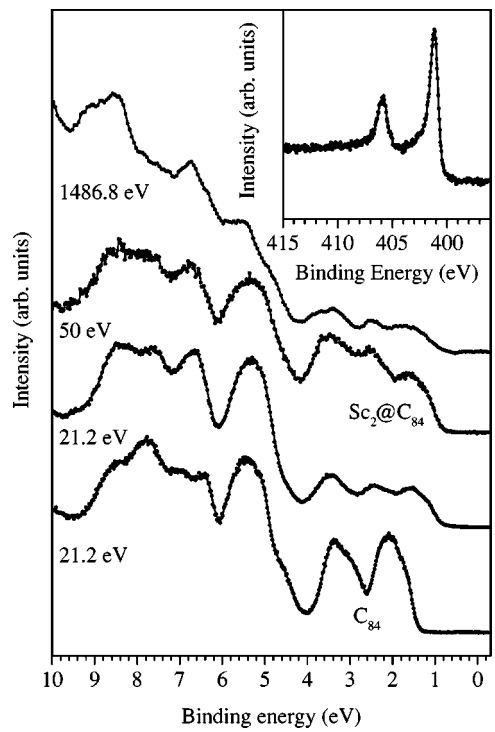

FIG. 1. Photoemission spectra of the D_{2d} isomer of $Sc_2@C_{84}$ at 21.2-, 50-, and 1486.6-eV photon energy and the He I (21.2 eV) photoemission spectrum of C_{84} (from Ref. 25). The inset shows the Sc $2p$ core-level doublets at 401.2 and 405.8 eV from XPS.

III. RESULTS AND DISCUSSION

As a first step we characterized our samples with regard to purity and possible contamination using XPS. The spectra of the $Sc_2@C_{84}$ film contained no contribution from the substrate, the remaining solvent, or any other contamination such as oxygen. All photoemission lines could be attributed to either Sc or C. In the valence-band region, to a first approximation, the matrix-element-weighted occupied density of states of the metallofullerene and low-lying core levels are probed. A comparison of the valence-band photoemission spectrum of the D_{2d} isomer of $Sc_2@C_{84}$ at 21.2, 50, and 1486.6 eV to the photoemission spectrum of C_{84} (from Ref. 25) at 21.2 eV is depicted in Fig. 1. C_{84} and $Sc_2@C_{84}$ are semiconductors with an onset of the highest occupied molecular orbital at 1.3 eV (Refs. 25 and 26) and 1 eV,[15] respectively. Taking into account that the transport gap is defined by the energy separation between the highest occupied molecular orbital in photoemission and the lowest unoccupied molecular orbital, as measured in an electron-addition experiment such as inverse photoemission, the measured 1-eV onset of the HOMO in Sc_2C_{84} gives a lower limit for the transport gap of the metallofullerene. The observed semiconducting behavior of $Sc_2@C_{84}$ is consistent with a closed-shell configuration, and thus with a charge transfer of two, four, or six electrons to the carbon cage.

A first hint of what the true charge transfer is can be found from an analysis of the photon energy dependence of the fine structure in the valence band. Compared to pristine C_{84}, two additional, pronounced structures at low binding energy are observed in the metallofullerene that had not been seen in earlier experiments.[15] These comprise a peak at 1.6

eV and a shoulder at 1.3 eV. These structures can be related either to charge transfer from the encaged Sc ions and the concomitant occupation of the unoccupied molecular orbitals of the C_{84} cage with D_{2d} symmetry, or to photoemission from remaining Sc $3d$ states following the charge transfer of less than three of the Sc valence electrons. The ratio between the atomic photoionization cross sections of C $2p$ and Sc $3d$ is about 6:3 at 21.2 eV and 1:3 for 1486.6 eV.[27] Thus any feature related to a Sc $3d$ photoemission should be enhanced by a factor of 10 in intensity when going from He I to Al $K\alpha$, which is not observed in the spectra. In a simple interpretation, the photon energy dependence of the valence-band spectra would argue against the presence of electrons in the Sc $3d$ levels–i.e., the Sc ions are trivalent. Although such a simple analysis is most probably able to distinguish between Sc in $3d^1$ and $3d^0$ states (i.e., $Sc^{3.0+}$ and $Sc^{2.0+}$), one should bear in mind that direct photoemission does not always give a full picture, and that resonant photoemission[21] or core-level excitation experiments[18] are more sensitive to the d-electron count, and therefore represent ideal methods with which to investigate this question in more detail—a question to which we will return shortly.

Returning to the photoemission data, in the inset to Fig. 1 we show the Sc $2p$ doublet. For Sc $2p$ XPS we find a peak at 401.2 eV for the $2p_{3/2}$ line, in agreement with the previously reported value.[15] However, the binding-energy shift of 1.8 eV to lower binding energy compared to the essentially ionic Sc_2O_3 cannot be explained unambiguously within an initial-state charging model by a change of the Sc valency, as the radically different screening environments in the final state between the oxide and the metallofullerene will certainly play a major role in the determination of the core-level binding energy observed in XPS.

As discussed above, the charge state of ions with localized electronic levels (such as $3d$ and $4f$ systems) can be extracted accurately from XAS experiments. For example, XAS at the Tm $4d$ edge of the metallofullerene $Tm@C_{82}$ was successfully used as a direct probe of the Tm valency in this system.[22,23] In the case of $3d$ transition-metal compounds, XAS of the $2p$ edge ($L_{2,3}$ XAS) can be used to easily identify different transition-metal valencies.[19,24] In Fig. 2 we show the result of the Sc $2p\rightarrow 3d$ x-ray absorption of a clean thin film of Sc2@C84 measured both at room temperature and at 50 K. Also shown are calculated multiplet distributions for the $3d^0\rightarrow 2p^5 3d^1$ and $3d^1\rightarrow 2p^5 3d^2$ transitions. These transitions represent (in the ionic limit) the Sc $L_{2,3}$ XAS for Sc^{3+} and Sc^{2+}, respectively. The calculated multiplet distributions were broadened to take into account of lifetime and resolution effects. From Fig. 2 it is clear that the XAS spectrum of ionic Sc^{3+} is simple, with two major peaks corresponding to the L_2 and L_3 edges. In contrast, for Sc^{2+}, a more complex spectrum is predicted, which arises from the interaction between the two $3d$ electrons in the final state, leading to stronger multiplet splitting in the XAS final state.

The experimental absorption spectra measured at room temperature and at 50 K closely resemble one another, both regarding their width, the L_2 to L_3 ratio (called the branching ratio), and even the overall shape. From this we can conclude that vibrational broadening resulting from the perturbation inherent in core ionization only has a minor effect on the

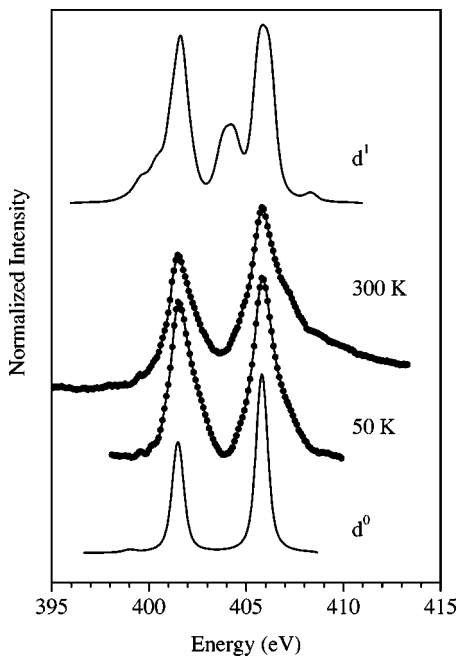

FIG. 2. Sc $2p\rightarrow 3d$ x-ray-absorption spectra of Sc2@C84 measured at room temperature and at 50 K. Below and above the spectra are the broadened calculated multiplet distributions for a $3d^0\rightarrow 2p^5 3d^1$ absorption (Sc^{3+}, $3d^0$ ground state), as well as for the $3d^1\rightarrow 2p^5 3d^2$ absorption (Sc^{2+}, $3d^1$ ground state).

width of the absorption lines. Once this point is clear, we can then compare the calculated and experimental XAS spectra, coming to the obvious conclusion that the calculated $3d^0$ ground-state configuration shows much better agreement with the observed spectra than the $3d^1$ ground state. Therefore, staying for the moment in a purely ionic picture, $Sc_2@C_{84}$ can be described formally as $(Sc^{3+})_2@(C_{84})^{6-}$.

A more detailed inspection of the calculated and experimental curves reveals, however, that the calculated multiplet spectrum for the $3d^0\rightarrow 2p^5 3d^1$ excitation of Sc^{3+} does not completely explain all the details of the experimental XAS spectra. For example, in addition to the main doublets at 401.5 and at 406 eV, there is a further fine structure in the specta with shoulders above the L_2 and L_3 edges. Furthermore, the branching ratio is not exactly reproduced by the calculations, and the experimental data are significantly broader than the theory, despite the fact that the latter are broadened to account for the finite core-hole lifetime (giving a broadening of $\approx$200 meV) and resolution (100 meV). Taken together, these factors indicate that a purely ionic picture is an oversimplification for this system, and that covalent interactions betwen the Sc ions and the carbon cage have to be taken into account.

To investigate the amount of covalency of the Sc(III) ions, more extended multiplet calculations, including charge transfer, have been performed, as mentioned above. For these calculations, a charge-transfer energy in the initial state $\Delta_{IS}=2$ eV and in the final state (i.e., after relaxation) $\Delta_{FS}=0$ eV have been used. For the hopping term T, which gives a measure of the hybridization between the carbon $2p$ and Sc $3d$ orbitals, the value used is 1 eV. This is significantly smaller than the the typical values used for calculations of transition metal oxides [$T\sim 2$ eV (Ref. 28)]. This

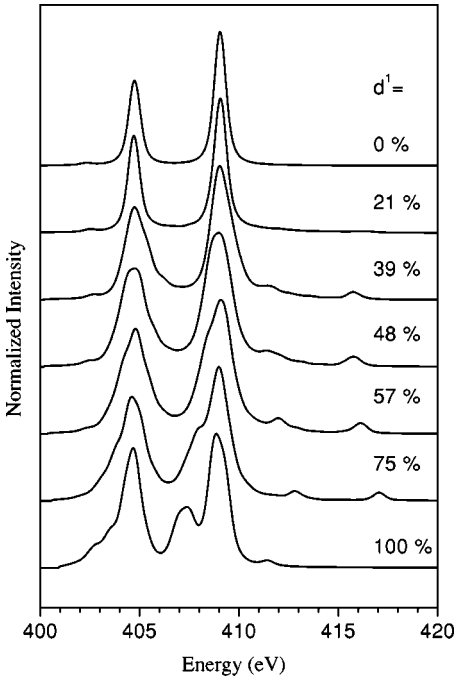

FIG. 3. Broadend calculated multiplet distribution for the Sc $2p \rightarrow 3d$ absorption edge including charge transfer using $\Delta_{IS} = 1$ eV and $\Delta_{FS} = 0$ eV, and for $T = 1$ eV. The numbers at the spectra give the percentage of the d^1 admixture in the calculations, respectively. For details, see the text.

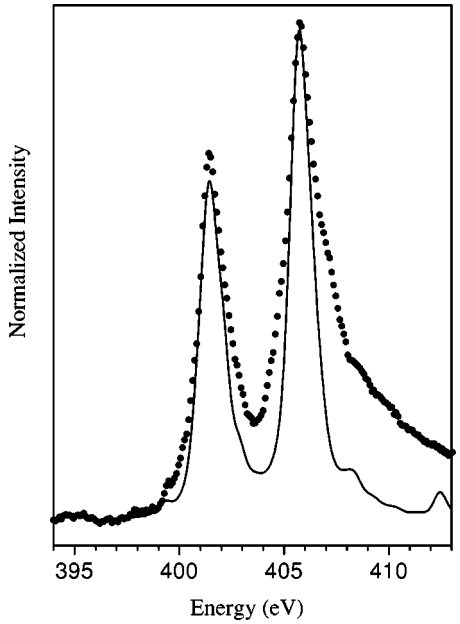

FIG. 4. Experimental high-resolution Sc $2p \rightarrow 3d$ x-ray-absorption spectrum measured at 300 K (●) compared to the calculated multiplet distribution that shows the best agreement with the experiment. In the calculation the Sc $3d^1$ admixture is 39%, leading to a formal Sc valence of 2.6+.

reduction is justified by the relatively weak hybridization between the carbon cage and the Sc ions which follows both from the predicted[16] and experimentally observed structure of the dimetallofullerene.[12] In these charge-transfer multiplet calculations, the effective formal valency of the encaged Sc ions is given by the ratio of the d^0 and d^1 contributions, which represent trivalent and divalent Sc, respectively. In order to better describe the envelope of possible cage-related electronic states which could donate charge to the Sc in the form of a covalent interaction, a finite bandwidth of the fullerene valence band involved in the hybridization was included by sampling five different $3d^1\underline{L}$ states, thus covering an effective bandwidth of about 4 eV. This figure is reasonable in light of the observed significant perturbation of the C $2p$-derived electronic states of, for example, C_{82} over about 4-5 eV, resulting from interaction with the endohedral La ion in $La@C_{82}$.[20]

The results of the calculations are depicted in Fig. 3 for different d^1 contributions, as indicated. As shown in Fig. 4, in comparison to the measured absorption spectrum, the intensity ratio between the L_2 and L_3 edges and the overall shape is best reproduced for the spectrum with a d^1 occupancy of 0.39 resulting in an effective valency of the encaged Sc(III) ions of 2.6 ± 0.1.

As it is clear that this result differs significantly from the Sc valency derived from earlier experiments on $Sc_2@C_{84}$ using either synchrotron x-ray diffraction or XPS, and indirectly from Raman spectroscopy, we point out that the data presented here are, to our knowledge, the first which directly, and site selectively probe the effective valence of the Sc ions in $Sc_2@C_{84}$ in a manner enabling an unambiguous extraction of the effective Sc $3d$ occupation number.

In detail, first the analysis of the Raman spectra in Ref. 14 was based upon a highly simplified model (the valence force model) that treats the complex $Sc_2@C_{84}$ molecule simply as three oscillators (two Sc and the C_{84}). Second, the refinement of the synchrotron x-ray-diffraction data in Ref. 12 was certainly accurate enough to elegantly prove the endohedral nature and the structure of the dimetallofullerene. However, this refinement, using the maximum entropy method might not possess the resolution necessary to distinguish between a situation in which each Sc ion has 0.8 or 0.39 $3d$ electrons given the electron density ''background'' arising from all the occupied C and Sc levels. Finaly, as discussed above, the initial-state charge model for the interpretation of core-level photoemission binding energies (''chemical shifts'')[15] is too crude to allow a derivation of the Sc valence with any certainty from a comparison of Sc systems with ligands of such different nature.

Following from the discussion above, it is apparent that the combined experimental and theoretical XAS investigations presented here give a direct probe of the effective d occupancy, as is evinced by numerous studies in the field of the transition-metal oxides. Thus, on the basis of these data, the effective charge transfer in the Sc dimetallofullerene is such to give a configuration $(Sc^{2.6+})_2@C_{84}^{5.2-}$.[29]

The reduced formal valency of the Sc(III) ions in $Sc_2@C_{84}$ illustrates that, in contrast to the divalent monometallofullerene $Tm@C_{82}$, a predominantly ionic picture is not applicable to this dimetallofullerene, and that covalent interactions between the encaged Sc ions and the C_{84} cage play an important role in the determination of the electronic structure. This is more like the picture arrived at from high-energy spectroscopic investigations of the trivalent monometallofullerene $La@C_{82}$, in which metal-fullerene hybridized states play an important role.

IV. CONCLUSION

In conclusion, we have presented a detailed study of the valence of the two Sc ions encapsulated in the D_{2d} isomer of C_{84} using high-energy spectroscopy. The multiplet structures in the Sc $2p$ x-ray-absorption spectrum prove unambiguously that the Sc ions in the dimetallofullerene $Sc_2@C_{84}$ are Sc(III). Furthermore, we have shown the applicability of the charge-transfer multiplet model for dealing with the covalent Sc-C interactions. Upon using this model to analyze the experimental data, we find the best agreement for a $3d^1$ admixture of 39% which allows us to pin down the effective valency of the Sc(III) ions to 2.6 ± 0.1. Our results clearly point out the importance of covalent interactions between the encaged Sc ions and the C_{84} cage in this dimetallofullerene. This is, for example, in contrast to the divalent monometallofullerene $Tm@C_{82}$.

Furthermore, the analysis presented here for the Sc valency in $Sc_2@C_{84}$ opens the way for a comparative study of the metal valency in the family of the Sc metallofullerenes. In this way, using a combination of XAS experiments with charge transfer calculations, the possible changes of the metal valency and in the covalent Sc-C interaction upon varying the number of encaged Sc ions from one up to four can be studied in detail, also enabling a systematic investigation of the influence of the Sc-Sc interactions on the electronic structure of these metallofullerenes.

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[29] The excellent agreement between theory and experiment presented here could be even further improved if the following additional factors were accounted for: the nonspherical nature of the C_{84} cage and the off-center position of the Sc ions (which result in abberations from the spherical crystal field); the nonrectangular shape of the C $2p$-based hybridization band; and the

possibility of a covalent interaction between the Sc ions themselves [which, upon consideration of the large separation of the Sc ions from one another (3.9 Å[12]) can be expected to play a minor role compared to the Sc-C covalency]. These factors, which are beyond the scope of the present paper, are expected mainly to lead to an additional broadening of the theoretically calculated multiplet distributions, but not to significant changes in the $3d$ count extracted from the theory.