Mixed valency in rare-earth fullerides

BY KOSMAS PRASSIDES*, YASUHiro TAKABAYASHI
AND TAKESHI NAKAGAWA

Department of Chemistry, University of Durham, Durham DH1 3LE, UK

Mixed-valence phenomena associated with the highly correlated narrow-band behaviour of the 4f electrons in rare earths are well documented for a variety of rare-earth chalcogenides, borides and intermetallics (Kondo insulators and heavy fermions). The family of rare-earth fullerenes with stoichiometry RE_{2.75}C_{60} (RE=Sm, Yb, Eu) also displays an analogous phenomenology and a remarkable sensitivity of the rare-earth valency to external stimuli (temperature and pressure) making them the first known molecular-based members of this fascinating class of materials. Using powerful crystallographic and spectroscopic techniques which provide direct indications of what is happening in these materials at the microscopic level, we find a rich variety of temperature- and pressure-driven abruptor continuous valence transitions—the electronically active fulleride sublattice acts as an electron reservoir that can accept electrons from or donate electrons to the rare-earth 4f/5d bands, thereby sensitively modulating the valence of the rare-earth sublattice.

Keywords: mixed valency; fullerenes; rare earths; valence transitions; synchrotron X-ray diffraction; X-ray absorption spectroscopy

1. Introduction

The high electron affinity of the C_{60} molecule and the weak intermolecular van der Waals forces in its crystalline form make solid C_{60} an excellent host for reductive intercalation chemistry. Indeed, intercalation of solid C_{60} with electron donors, such as the alkali, alkaline-earth and rare-earth metals, has resulted in a wealth of fulleride salts with stoichiometries A_{x}C_{60}, where the dopant level \( x \) could be as low as 1 (e.g. RbC_{60}) or as high as 12 (e.g. Li_{12}C_{60}). Changing the size and nature of the dopants affects the structural and electronic properties of the materials sensitively. Among the most well-known derivatives of C_{60} are those with alkali metals and stoichiometry A_{3}C_{60}, which are metallic and become superconducting with high transition temperatures, \( T_{c} \) (up to 33 K at ambient pressure). These salts adopt, in general, either FCC or primitive cubic structures in which the three cations occupy the available octahedral and tetrahedral interstitial sites. Charge transfer is essentially complete and the conduction band of C_{60}, which arises from its lowest unoccupied molecular orbital (LUMO) of \( t_{1u} \) symmetry, is half filled. A striking feature of these materials emerges when the magnitudes of the on-site Coulomb repulsion, \( U \), and the \( t_{1u} \) bandwidth, \( W \), are

* Author for correspondence (k.prassides@durham.ac.uk).

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compared (Margadonna & Prassides 2002; Durand et al. 2003; Iwasa & Takenobu 2003; Margadonna et al. 2004). The estimate of $U$ for the C$_{60}$ molecule is of the order of 3 eV but this value is reduced in the solid to approximately 1 eV. Still it is much larger than the typical values of $W$ for A$_3$C$_{60}$ (approx. 0.5 eV), rendering the $(U/W)$ ratio much greater than 1. Under these circumstances, a transition to a Mott–Hubbard insulating state is expected. However, metallic behaviour survives by virtue of the triple orbital degeneracy of the $t_{1u}$ LUMO state which shifts the boundary of the metal–insulator transition to a critical value of $(U/W)_c \approx 2.5$ (Gunnarsson 2004). As a result, the metallic fulleride phases can be considered as archetypal highly correlated molecular systems with electron correlations playing a crucial role in determining the normal and superconducting state properties (cf. high-$T_c$ superconducting cuprates, colossal magnetoresistive manganites). In the alkali fulleride phases, the metal ions residing in the interstitial spaces of the C$_{60}$ structure are electronically innocent and the electronic properties are entirely determined by those of the C$_{60}^{3-}$ sublattice. A comparable situation is encountered for alkaline-earth fullerides in which partial occupation of the LUMO $t_{1g}$-derived band also leads to metallic and superconducting compositions for various levels of band filling (Brown et al. 1999; Margadonna et al. 2000). The main important difference here is the occurrence of hybridization between alkaline-earth and C orbitals in contrast to the alkali metal fullerides where full charge transfer from the metals to C$_{60}$ occurs.

The rare-earth fulleride chemistry is not as widely established as that of the alkali and alkaline-earth metals. Nonetheless, the introduction of electronically active cations in the void spaces of the C$_{60}$ lattice offers intriguing possibilities of interesting electronic and magnetic behaviour that may result from the coupling of the two electronically active sublattices and therefore the electronic states of rare-earth fullerides deserve careful investigation. For instance, given that the rare-earth dopants may carry a magnetic moment, this strategy has been used in the synthesis of molecular magnetic materials. Prominent examples of such behaviour include the ferromagnetic fullerides, Eu$_6$C$_{60}$ and Eu$_9$C$_{70}$, with Curie temperatures of 14 and 40 K, respectively (Ishii et al. 2002; Margiolaki et al. 2002; Takenobu et al. 2003). Magnetic correlations in these systems develop either through direct exchange interactions between the Eu$^{2+}$ ($4f^7$) ions or through p–d, f interactions mediated by the fulleride units.

We also recall here that the chemistry of the rare-earth elements is typically dominated by the +3 oxidation state. Well-established exceptions include Ce, Sm, Eu, Tm and Yb, for which the +4 or +2 oxidation states can be also stabilized in their compounds (Strange et al. 1999). Of particular interest in such circumstances are selected rare-earth systems (Kondo insulators and heavy fermions) for which the 4f levels lie close to the Fermi level, $E_F$, and may exhibit the phenomenon of mixed (or intermediate) valence (Wachter 1994; Malterre et al. 1996). The groundstate of MV solids such as SmS, SmB$_6$ and YbB$_{12}$ has been rationalized phenomenologically in terms of the valence fluctuation model of two nearly degenerate electronic configurations, 4f$^n$5d$^0$ and 4f$^{n-1}$5d$^1$ (or theoretically by the one-impurity Anderson model). The hybridization strength between the localized 4f and the conduction 5d electrons can be tuned by both chemical substitution and the application of pressure. Unambiguous signatures of electronically driven valence changes with changes in external
stimuli (temperature, pressure) are found in the variation of the elastic properties of MV rare-earth solids; anomalous expansion coefficients (abrupt or quasi-continuous lattice collapse or inflation) without changes in crystal structure—attributed to the differing radii of the $4f^n$ and $4f^{n-1}$ ions ($r(4f^n) > r(4f^{n-1})$)—accompany the rare-earth valence transitions (Jayaraman et al. 1970, 1973; Lawrence et al. 1996; Alekseev et al. 2006). In these mixed-valence phases, the electronic properties are entirely determined by the unconventional strongly correlated character of the cationic rare-earth sublattice as invariably the anionic sublattices comprise closed-shells units and are electronically inactive. Therefore, the family of rare-earth fullerides in which the narrow $C_{60}$ $t_{1u}$ band with its strongly correlated nature is in close proximity to the rare-earth 4f and 5d bands potentially offers particularly intriguing possibilities to realize novel electronic behaviour when compared with other known mixed-valence solids (Kondo insulators) such as the samarium chalcogenides.

2. Crystal structures of rare-earth fullerides, RE$_{2.75}$C$_{60}$

(Re = Sm, Yb, Eu)

Unlike the alkali and alkaline-earth fullerides, in which cubic line phases with stoichiometry $A_3C_{60}$ and fully occupied tetrahedral and octahedral interstices play a dominant role in their chemistry, reactions of rare-earth metals with fullerenes (Chen & Roth 1995; Özdas et al. 1995) lead to compositions with the chemical formula RE$_{2.75}$C$_{60}$ (RE = Sm, Yb, Eu). Early claims of the appearance of superconductivity (Chen & Roth 1995; Özdas et al. 1995) for these phases were later established to be incorrect (Claves & Hamwi 2000; Arvanitidis et al. 2003, 2004). Their crystal structures are orthorhombic (space group $Pcab$; $b > a > c$) with the rare-earth cations occupying off-centred tetrahedral and octahedral interstitial sites (Özdas et al. 1995). One out of every eight tetrahedral sites is partially occupied (less than 25%) and a long-range ordering of these tetrahedral defects results in a unit cell with dimensions in all three directions twice as large as those of the commonly encountered FCC alkali fulleride structures (unit cell volume: $V_{ortho} \approx 8V_{FCC}$). In addition, the structural model is characterized by large displacements of the cations from the centres of the octahedral sites ($\approx 2.3$ Å) and smaller displacements from the centres of the tetrahedral sites ($\approx 0.4$ Å). The five symmetry-inequivalent $C_{60}$ units present in the unit cell ($C_{60}(1)$ at $(0 \ 0 \ 0)$, $C_{60}(21)$ at $(0 \ 1/4 \ 1/4)$, $C_{60}(22)$ at $(1/4 \ 0 \ 1/4)$, $C_{60}(23)$ at $(1/4 \ 1/4 \ 0)$ and $C_{60}(3)$ at $(1/2 \ 1/2 \ 1/2)$) are rotated anticlockwise by 37.5° about local symmetry axes ([111], [111], [111], [111] and [111], respectively). To define the 32 $C_{60}$ units present in the unit cell, 240 independent C atoms are needed (figure 1). No unusually short RE–C contacts are present with the average RE–C distances being of the order of 2.9 Å (Arvanitidis et al. 2003).

3. Pressure-induced valence transition in Sm$_{2.75}$C$_{60}$

The sensitivity of the Sm$_{2.75}$C$_{60}$ structure to the application of pressure (up to 6.03 GPa) was investigated by synchrotron X-ray powder diffraction measurements at ambient temperature. As the external pressure increases initially, the
unit cell contracts monotonically. However, upon reaching a pressure of 3.95 GPa, an abrupt phase transformation sets in to a structure with drastically reduced lattice dimensions. The large lattice collapse ($\Delta V / V \sim 6\%$) is complete at 4.72 GPa. The phase transformation is found to be both reversible and characterized by a large hysteresis as the original low-pressure phase does not recover until pressure well below 3.45 GPa is reached (figure 2). The pressure-induced phase transition is also accompanied by a (reversible) colour change of the material from black to golden implying a concomitant change in the conducting properties—an insulator-to-metal transition (Arvanitidis et al. 2004).

In order to rationalize the collapse of the Sm$_{2.75}$C$_{60}$ unit cell metrics with increasing pressure, we recall the behaviour of the archetypal Kondo insulating systems, samarium monochalcogenides. For instance, SmS which adopts a NaCl-type structure undergoes a similar abrupt (first-order) isosymmetric catastrophic transition ($\Delta V / V \sim 16\%$) from a semiconducting black phase to a metallic gold one at 0.65 GPa at ambient temperature (Jayaraman et al. 1970; Barla et al. 2004; Deen et al. 2005). This behaviour has been explained in terms of a pressure-induced electron transfer from Sm$^{2+}$($4f^6$) localized states into the...
Sm$^{2+}$ (4f$^5$5d$^1$) conduction-band states—at ambient pressure, the Sm ions are nearly divalent but above 0.65 GPa, the Sm 5d and 4f bands begin to overlap and the 4f electrons spill into the 5d band and the Sm ions are in a mixed-valent Sm$^{2+}$/Sm$^{3+}$ metallic state with an average valence of approximately 2.5–2.7. The lattice collapse reflects the drastically decreased ionic size of the Sm ions upon increasing the valence. Such a 4f$\leftrightarrow$5d electron delocalization also provides an excellent description of the behaviour of Sm$_{2.75}$C$_{60}$ with increasing pressure. At ambient pressure, we can obtain an estimate of the average Sm valence by magnetic susceptibility measurements. The room-temperature value of the magnetic susceptibility of Sm$_{2.75}$C$_{60}$ ($\chi_{RT} = 3.75 \times 10^{-3}$ emu (mol Sm)$^{-1}$) straddles those calculated for the free Sm$^{2+}$ and Sm$^{3+}$ ions (Arvanitidis et al. 2003). At sufficiently high temperatures in mixed-valence compounds, the measuring scale is faster than the fluctuation rate between the two valence configurations and the magnetic susceptibility is expected to be a linear combination of the Sm$^{2+}$ and Sm$^{3+}$ contributions, $\chi_{RT} = (1-\varepsilon)\chi(\text{Sm}^{2+}) + \varepsilon\chi(\text{Sm}^{3+})$. This provides an estimate of the average Sm valence ($2+\varepsilon$) as approximately equal to $+2.2$ to $2.3$. As the pressure increases, the gap between the $t_{1u}$ band of C$_{60}$ and the Sm 5d conduction band decreases until at the critical pressure of approximately 4 GPa, they overlap allowing the 4f electron density to spill over into the 5d band. This leads to an increase in the average Sm valence towards $+3$, a decrease in the size of the rare-earth ion (i.e. a decrease in the unit cell size) and a transition to a metallic state.

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4. Temperature-induced valence transitions in RE$_{2.75}$C$_{60}$
(RE=Sm, Yb, Eu)

(a) Structural response and negative thermal expansion

The structural properties of the orthorhombic RE$_{2.75}$C$_{60}$ (RE=Sm, Yb, Eu) systems and the isostructural alkaline-earth fulleride Ca$_{2.75}$C$_{60}$ were studied as a function of temperature between 5 and 300 K by high-resolution synchrotron X-ray powder diffraction. The striking feature of the temperature dependence of the diffraction data for all the rare-earth fullerides (Arvanitidis et al. 2003; Margadonna et al. 2005) is that the angular positions of the diffraction peaks shift significantly in a continuous fashion to higher values as the temperature increases above 5 K, implying an anomalous structural behaviour whereby the unit cell metrics decrease continuously with increasing temperature and the thermal expansivity, $\alpha_V (=-\ln V/dT)$, which approaches values as high as $-1000$ ppm K$^{-1}$ is negative. This behaviour is not accompanied by any observable change in crystal symmetry. The overall decrease in lattice size on heating is 0.84% for Sm$_{2.75}$C$_{60}$, 1.40% for Yb$_{2.75}$C$_{60}$ and 0.85% for Eu$_{2.75}$C$_{60}$. The anomalous lattice response disappears above a characteristic critical temperature for each rare-earth fulleride ($T_V$=32 K for Sm$_{2.75}$C$_{60}$, 60 K for Yb$_{2.75}$C$_{60}$ and 90 K for Eu$_{2.75}$C$_{60}$), and the lattice constants increase on further heating to room temperature (figure 3). Nonetheless, it is remarkable that for all these systems the lattice expansion in the high-temperature regime is still not large enough to produce a cell volume at ambient temperature comparable to that at 5 K. In contrast, the alkaline-earth fulleride, Ca$_{2.75}$C$_{60}$ shows no anomalous expansion behaviour, exhibiting a positive thermal expansivity throughout and a lattice expansion between 5 and 300 K of approximately 0.55% (figure 3c).

The temperature evolution of the lattice parameters is a powerful and direct indicator of what is happening in these materials at the microscopic level. The anomalous response of the RE$_{2.75}$C$_{60}$ lattice size at low temperature without an accompanying change in crystal symmetry can be rationalized in terms of the average RE oxidation state approaching +2 upon cooling below the critical temperature, $T_V$ (Arvanitidis et al. 2003; Margadonna et al. 2005). As the valence decreases, the RE ionic radius increases continuously and the materials display negative thermal expansion coefficients. The large magnitude of the volume inflation, despite the small rare-earth valence change may be understood if we note that the tetrahedral hole in RE$_{2.75}$C$_{60}$ has a radius of 1.12 Å, straddling the values of the ionic radii of RE$^{2+}$ and RE$^{3+}$, and therefore, even small changes in valence have a profound effect on the lattice size. We also propose that the driving force of the valence change is electronic in origin and is inherently connected with the details of the electronic band structures of these systems. At high temperatures, 4f electrons can be thermally excited from the narrow 4f band into the C$_{60}$ t$_{1u}$ band. At low temperatures, these electrons are taken back into the 4f band resulting in a RE$^{2+}$ electronic configuration and an expanded ionic radius. Consistent with this picture, no lattice anomalies are observed for the isoelectronic and isostructural Ca$_{2.75}$C$_{60}$ fulleride, which lacks an electronically active 4f sublattice.

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Probing the rare-earth valence directly

Direct experimental information about the valence states of the rare-earth ions in the fulleride salts can be sought using element-specific spectroscopic techniques. Indeed, X-ray absorption spectroscopy (XAS) at the rare-earth metal $L_3$ absorption edges has been successfully employed before to follow the evolution of the rare-earth valence with changes in temperature and pressure for various Kondo insulators (Beaurepaire et al. 1990). In such total fluorescence yield experiments, the integrated scattered intensity recorded as the incident energy, $h\nu_{in}$, varies through the $L_3$ absorption edge. For mixed-valence systems, two features are typically observed; these correspond to transitions from the mixed-valence groundstate (e.g. for a Sm system: $|\Psi_g\rangle = \alpha|\text{Sm}^{2+}\rangle + \beta|\text{Sm}^{3+}\rangle$) to final states of $2p^54f^6$ and $2p^54f^5$ character, split in energy by the Coulomb interaction with the $2p$ core hole. The relative intensity of the features provides a

Figure 3. Temperature evolution of the unit cell volume in (a) Sm$_{2.75}$C$_{60}$, (b) Yb$_{2.75}$C$_{60}$ and (c) Ca$_{2.75}$C$_{60}$.

(b) Probing the rare-earth valence directly

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direct measure of the average rare-earth valence in the material. The spectral contributions of the two transitions are better resolved in the high-resolution partial fluorescence yield (PFY) spectra, where the intensity of the $L_\alpha_1$ de-excitation ($2p^53d^{10} + h\nu_{\text{in}} \rightarrow 2p^63d^9 + h\nu_{\text{out}}, h\nu_{\text{out}} = 5636 \text{ eV}$) is recorded as the incident energy varies through the Sm $L_3$ edge. The improved resolution arises from the sharpening of the spectral features due to the longer lifetime of the shallower 3d hole when compared with that of the deep 2p hole (Dallera et al. 2002; Annese et al. 2006; Moreschini et al. 2007).

The PFY spectra of the (Sm$_{2/3}$Ca$_{1/3}$)$_{2.75}$C$_{60}$ fulleride were measured as a function of temperature between 4 and 300 K (A. Tamai et al. 2007, unpublished data). Two main structures are observed at 6713 and 6722 eV and assigned to the Sm$^{2+}$ and Sm$^{3+}$ components, respectively, thereby validating the presence of mixed valency in this rare-earth fulleride (figure 4). The relative intensity of the two components at 300 K implies that the average valence state of the Sm ion is closer to +2 than to +3. In addition, the temperature evolution of the relative intensities, $I$(Sm$^{n+}$), of the Sm$^{2+}$ and Sm$^{3+}$ features provides a clear qualitative evidence that a sharp first-order valence transition (Sm$^{2+} \rightarrow$ Sm$^{3+}$) occurs on cooling below $T_v \approx 20$ K to a state with increased Sm$^{2+}$ character, as signified by the abrupt increase in the spectral weight of the Sm$^{2+}$ feature. This is entirely consistent with the evidence provided by the structural data and the observation of negative thermal expansion effects at low temperature. However, what is remarkable from these measurements is also the unambiguous observation that the $I$(Sm$^{2+}$)/$I$(Sm$^{3+}$) ratio decreases in a continuous fashion below 300 K.

Figure 4. Temperature dependence of the PFY–XAS spectra of (Sm$_{2/3}$Ca$_{1/3}$)$_{2.75}$C$_{60}$ between 4 and 300 K. The features at 6713 and 6722 eV are due to the Sm$^{2+}$ and Sm$^{3+}$ components, respectively, of the $L_\alpha_1$ de-excitations and the spectral intensities are normalized to those at 6713 eV. The inset shows a close-up view of the Sm$^{3+}$ component at 4, 50 and 275 K.
implying that the average Sm valence increases monotonically on cooling towards \( T_v \) whence an abrupt phase transition occurs and the Sm state collapses to valence values even smaller than those at ambient temperature (figure 4 inset).

The complex temperature evolution of the Sm valence states was also probed by using the resonant inelastic X-ray scattering (RIXS) technique. In the RIXS process, final Sm electronic states of mainly \( 3d^94f^5 \) and \( 3d^94f^6 \) character are reached radiatively from the XAS final states; for each value of \( \hbar \nu_{\text{in}} \), the whole energy distribution of the emitted photons is recorded over a broad (\( \hbar \nu_{\text{in}}, \hbar \nu_{\text{out}} \)) parameter space and the \( \text{Sm}^{2+} \) and \( \text{Sm}^{3+} \) contributions are selectively and resonantly enhanced by tuning the excitation energy (Dallera et al. 2002; Annese et al. 2006; Moreschini et al. 2007).

The results obtained are in excellent agreement with those from the PFY–XAS measurements. At ambient temperature, the average valence state of Sm in the \((\text{Sm}_{2/3}\text{Ca}_{1/3})_{2.75}\text{C}_{60}\) fulleride is approximately \(+2.20\). On cooling, the \( I(\text{Sm}^{3+})/I(\text{Sm}^{2+}) \) ratio of the \( \text{Sm}^{3+} \) and \( \text{Sm}^{2+} \) features in the RIXS spectra continuously increases in intensity signifying a decrease in the Sm 4f occupation number and an increase in the average valence which approaches a maximum value of approximately \(+2.28\) at 20 K (A. Tamai et al. 2007, unpublished data). Below \( T_v \approx 20 \text{ K} \), a sudden valence change occurs and the Sm 4f occupation number abruptly increases leading to an average valence of approximately \(+2.19 \text{ K}\) at 4 K (figure 5).

5. Conclusions

The evolution of the structural and electronic properties of mixed-valence rare-earth fullerides with stoichiometry \( \text{RE}_{2.75}\text{C}_{60} \) (\( \text{RE} = \text{Sm}, \text{Yb}, \text{Eu} \)) has been studied by synchrotron X-ray diffraction and absorption techniques. The temperature-
dependent crystallographic studies reveal the abrupt onset of large lattice expansion (negative thermal expansion) on cooling below a critical temperature, $T_v$ (32 K for Sm, 60 K for Yb and 90 K for Eu), thereby providing unambiguous signatures of temperature-induced RE$^{3+} \rightarrow$RE$^{2+}$ valence transitions of the RE ions. The transformations are of electronic origin and are driven by the coupling of the RE 4f band and the t$_{1u}$ band of C$_{60}$. As expected, they are absent when the electronically active 4f sublattice is missing in the related alkaline-earth fulleride, Ca$_{2.75}$C$_{60}$. Complementary X-ray absorption and RIXS measurements on the (Sm$_{2/3}$Ca$_{1/3}$)$_{2.75}$C$_{60}$ fulleride confirm the electronic nature of the low-temperature first-order valence transition but additionally reveal a continuous decrease in the 4f electron occupation number (Sm$^{2+}$ $\rightarrow$ Sm$^{3+}$) on cooling from ambient temperature down to $T_v$. The rare-earth valence states are also found to be fragile upon compression and a pressure-induced first-order (reversible) RE$^{2+} \rightarrow$RE$^{3+}$ transition, accompanied by a lattice collapse and a change in colour (insulator-to-metal transition) is observed at approximately 4 GPa. The observed experimental phenomenology is reminiscent of that of highly correlated Kondo insulators such as SmS and YbInCu$_4$, but the simultaneous presence of the electronically active fulleride sublattice which can act as an electron reservoir, accepting electrons from or donating electrons to the rare-earth 4f/5d bands with changes in temperature or pressure leads to a more complex electronic behaviour.

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