Raman spectroscopic study of the rare-earth fullerides Eu$_{6-x}$Sr$_x$C$_{60}$†‡

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We present Raman spectroscopic studies of the isostructural and isoelectronic Eu$_{6-x}$Sr$_x$C$_{60}$ ($x = 0, 3, 5, 6$) and Ba$_6$C$_{60}$ compounds. The Raman spectra of the Eu-based fullerides show dramatic changes compared to the pure alkaline-earth systems, including significant broadening, splitting and frequency shifts of the fivefold degenerate H$_{1g}$ intramolecular modes of C$_{60}$. Moreover, the A$_g(2)$ mode exhibits an even larger downshift and a remarkable broadening. These findings are consistent with distortions of the C$_{60}$ molecular cages and a considerable electron-phonon coupling strength—strongly enhanced in the Eu containing systems—originating from the strong orbital hybridization between the metal atom and the C$_{60}$ molecule.

Introduction

Rare-earth C$_{60}$ fullerides—metal intercalation compounds of C$_{60}$—constitute an intriguing class of novel highly-correlated molecular systems due to the strong coupling between two electronically active sublattices {π(C$_{60}$) and 4f,5d(rare-earth)}. Doping C$_{60}$ fullerite with lanthanide ions carrying a magnetic moment can lead to novel magnetic molecular materials as magnetic correlations may develop either through direct exchange between the lanthanides or through the C$_{60}$ molecules by π–d$^f$ interactions. In this context, the body-centred cubic (bcc) Eu$_{6-x}$Sr$_x$C$_{60}$ ($x = 0, 3, 5$) compounds undergo transitions to ferromagnetic states below 10–14 K, while the exact Eu content does not affect considerably the Curie temperature, $T_C$. The magnetic structure of the Eu$_6$C$_{60}$ fulleride has been determined by powder neutron diffraction measurements. The significant π(C$_{60}$)-d$_f$(Eu) orbital interactions modulate the magnetic exchange and can explain the conducting and giant magnetoresistive properties of this system. The strong orbital mixing between the metal atom and the C$_{60}$ π states is reminiscent of the situation encountered in the alkaline-earth fullerides, Ba$_6$C$_{60}$ and Sr$_6$C$_{60}$. In these systems, hybridization of the C$_{60}$ and the alkaline-earth atom electronic states also leads to metallic behaviour, despite the nominally complete filling of the $t_{1g}$ band. The hybridization acts in synergy with the electrostatic attractive interaction and shortens significantly the interfullerene separation (shorter in Sr$_6$C$_{60}$ than in Ba$_6$C$_{60}$). Thus, in these alkaline-earth fullerides the density-of-states at the Fermi level increases with decreasing interfullerene distance, contrary to what is established for the metallic alkali fullerides M$_3$C$_{60}$.

Raman scattering, which probes mainly the intramolecular C$_{60}$ modes, is a powerful tool in the investigation of fulleride properties thanks to its sensitivity to the local structural and electronic perturbations. Therefore, here we employ Raman spectroscopy to study the structural characteristics of the molecular cages and the metal-C$_{60}$ hybridization effects in the Eu$_{6-x}$Sr$_x$C$_{60}$ family in comparison to those of the isostructural and isoelectronic Ba$_6$C$_{60}$ system.

Experimental

Samples were prepared by reaction of stoichiometric quantities of C$_{60}$, Eu, and Sr powders at 500 °C for 5 days and at 600 °C for 3 days with an intermediate grinding.

Powder X-ray diffraction (XRD) and magnetic susceptibility measurements showed the phase purity of the samples. This was also confirmed by the well-resolved Raman spectra and the appearance of a single peak in the frequency region of the A$_g(2)$ intramolecular mode of C$_{60}$ (Fig. 1).

Raman spectra were recorded in the back-scattering geometry using a JASCO NRS-1000 and a DILOR XY micro-Raman...
system, both equipped with CCD detectors. For excitation, the 632.8 nm line of a He–Ne laser was focused on the sample by means of a 100x objective lens with a spot diameter of ~1 µm, while the laser power was kept below 0.01 mW in order to eliminate laser-heating effects and the concomitant softening of the intramolecular C\textsubscript{60} modes.

Results and discussion

In C\textsubscript{60} fullerides, the charge transfer from the metallic atoms to the molecular cages as well as the lowering of the crystal and the molecular symmetry cause frequency shifts of the Raman peaks, splitting of the fivefold degenerate H\textsubscript{g} modes and the activation of silent -in the icosahedral molecular symmetry, I\textsubscript{h} - modes.\textsuperscript{5,6} Thus, the Raman spectrum of the studied compounds is richer in structure compared to that of pristine C\textsubscript{60} (Fig. 1). The peak frequencies and linewidths of the intramolecular C\textsubscript{60} modes in the Eu\textsubscript{6}, A\textsubscript{3}C\textsubscript{60} (A = Sr, Ba; x = 0, 3, 5, 6) fullerides, obtained by Lorentzian fits to the experimental data, are summarized in Table S1 of the ESI\textsuperscript{†}.\textsuperscript{7} The frequencies of the relatively strong Raman peak related to the A\textsubscript{3}(2) pentagonal-pinch mode and the A\textsubscript{3}(1) radial breathing mode of the C\textsubscript{60} molecule are similar for all the studied systems, consistent with a divalent state for the Eu ions. This is in agreement with the results of X-ray absorption near-edge structure (XANES) studies, as well as with the magnetic moment values per Eu ion obtained from magnetic susceptibility data of the Eu-based fullerides with Ln\textsubscript{x}C\textsubscript{60} stoichiometry or from powder neutron diffraction measurements of Eu\textsubscript{6}C\textsubscript{60}\.\textsuperscript{7,8}

In the alkaline-earth fullerides Ba\textsubscript{x}C\textsubscript{60} and Sr\textsubscript{x}C\textsubscript{60}, the low-frequency intramolecular H\textsubscript{g}(1) and H\textsubscript{g}(2) modes appear to split into two and four components, respectively (Fig. 2). The frequencies of the split components are the same, within experimental accuracy, to those earlier reported for Ba\textsubscript{x}C\textsubscript{60}, where a fifth H\textsubscript{g}(2) peak has been also observed.\textsuperscript{7} However, the splitting of the H\textsubscript{g}(2) mode (as well as the appearance in our spectra of three peaks for both the H\textsubscript{g}(3) and the H\textsubscript{g}(5) modes) is inconsistent with the considerations of group theory that predicts a splitting into two peaks (H\textsubscript{g} → E\textsubscript{g} + F\textsubscript{g}) for the Im\textsubscript{3} space group (I\textsubscript{h} point group) of the bcc A\textsubscript{6}C\textsubscript{60} fullerides.\textsuperscript{6} The additional splitting of degenerate intramolecular modes with respect to theoretical predictions has also been observed by means of Raman and infrared spectroscopy in alkali fullerides with stoichiometries M\textsubscript{3}C\textsubscript{60} and M\textsubscript{6}C\textsubscript{60}, where it was attributed to the molecular Jahn–Teller effect.\textsuperscript{8,9} However, such a mechanism is unlikely for the case of fullerides with a completely filled conduction band. Therefore, the peculiar splitting of various intramolecular modes with the H\textsubscript{g} symmetry in the alkaline-earth fullerides Ba\textsubscript{x}C\textsubscript{60} and Sr\textsubscript{x}C\textsubscript{60} suggests a possible symmetry lowering undetectable by XRD measurements.\textsuperscript{7} A C\textsubscript{60} molecular distortion has been also reported recently in the case of the isostructural M\textsubscript{6}C\textsubscript{60} (M = Rb, Cs) alkali fulleride, attributed to the Coulombic interaction between the fullerene anion and the intercalated cations.\textsuperscript{10,11} This deformation is analogous to pulling the molecule through the three orthogonal axes pointing towards the bcc faces containing the alkali metals and is strongly enhanced upon pressure application and the consequent reduction of the unit cell volume.

In Eu\textsubscript{x}C\textsubscript{60} and the mixed Eu\textsubscript{x}, Sr\textsubscript{y}C\textsubscript{60} fullerides where Sr is substituted by the quite similarly sized Eu ion, the splitting of the H\textsubscript{g} modes becomes much more pronounced; a fifth component of the H\textsubscript{g}(2) mode appears in the spectrum while the H\textsubscript{g}(1) mode -comprising two components in Ba\textsubscript{x}C\textsubscript{60} and Sr\textsubscript{x}C\textsubscript{60} - splits into four peaks (Fig. 2). A similar splitting has been observed in Ba\textsubscript{6}C\textsubscript{60} fulleride that was attributed, however, to its lower crystal symmetry (orthorhombic).\textsuperscript{7} In addition, the Raman peaks of the Eu based fullerides—and particularly the peaks originating from C\textsubscript{60} modes with an increased tangential character—broaden significantly compared to that of the pure alkaline-earth fullerides (see also Table S1 in the ESI\textsuperscript{†}). These effects are consistent with a stronger Eu-C\textsubscript{60} orbital mixing that distorts the surface regularity of the molecular cages. Moreover, as the electron-phonon coupling broadens considerably the Raman peaks in metallic systems like the A\textsubscript{3}C\textsubscript{60} alkali fullerides,\textsuperscript{12} the more prominent broadening of the intramolecular C\textsubscript{60} modes in the Eu\textsubscript{x}, Sr\textsubscript{y}C\textsubscript{60} (x = 0, 3, 5) compounds could be also suggestive of enhanced metallic character compared to the pure alkaline-earth fullerides. Note, however, that in these compounds—similarly to the case of Ba\textsubscript{x}C\textsubscript{60}—the proportional linewidth vs. line shift relation observed for the metallic K\textsubscript{3}C\textsubscript{60} and Ba\textsubscript{3}C\textsubscript{60} fullerides does not hold, rendering the applicability of Allen’s theory for electron-phonon coupling in Eu based fullerides questionable.\textsuperscript{7,8}

It is interesting to compare the Raman spectrum of the multinary Eu\textsubscript{x}, Sr\textsubscript{y}C\textsubscript{60} compounds with that of the isostructural Sm\textsubscript{3}C\textsubscript{60} rare-earth fulleride having also a completely filled f\textsubscript{t5} band. In the Sm fulleride, the similarity in the frequencies of the
Ag modes with those of the A$_6$C$_{60}$ alkaline-earth fullerides also revealed the divalent state of the Sm ions. This suggests a common behaviour of the rare-earth valence for the completely filled conduction band, contrary to the intermediate valence state (2 + $\epsilon$) + adopted by the lanthanide ions in the other stable stoichiometry of the rare-earth fullerides with almost filled $t_{1u}$ band, the Ln$_{2.75}$C$_{60}$ systems. In addition, the splitting of the H$_g$(1) and the H$_g$(2) modes into three and five components, respectively, in Sm$_6$C$_{60}$ has been attributed to the strong coupling between Sm and C$_{60}$, resulting—as in the case of the Eu$_6$C$_{60}$ compounds studied here—in a structural distortion of the molecular cages. This assumption is also confirmed by the short nearest-neighbour molecular separation and the metallic behaviour of the Sm$_6$C$_{60}$ system.

In C$_{60}$-based fullerene systems, the frequency of the Raman peak associated with the tangential A$_g$(2) mode of the C$_{60}$ molecule ($\sim$1468 cm$^{-1}$ in C$_{60}$ fullerite) is also of great importance as it is extremely sensitive to external perturbations like pressure, temperature, intermolecular bonding and doping. In alkali fullerides, this peak exhibits a downshift of 6–7 cm$^{-1}$ per electron transferred from the metal atoms to the C$_{60}$ molecule, attributed to the elongation of the intramolecular bonds induced by the charge transfer process and the resulting softening of the force constants. A larger downshift of the pentagonal-pinch mode is observed in Ba$_6$C$_{60}$ (with $t_{1g}$ states) that is attributed to the metal-C$_{60}$ coupling and their orbital hybridization. The frequency and the width of the Raman peak associated with the A$_g$(2) intramolecular mode in the studied fullerides are illustrated in Fig. 3 as a function of their unit cell volume. As it can inferred from this figure, the A$_g$(2) mode softening becomes more

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**Fig. 2** Raman spectra in the frequency region of (a) the H$_g$(1) and (b) the H$_g$(2) intramolecular mode for the Eu$_{6-x}$A$_x$C$_{60}$ (A = Sr, Ba; x = 0, 3, 5, 6) fullerides. Dashed curves indicate Lorentzian-type deconvolution of the spectra, while the vertical lines mark the split components.

**Fig. 3** Frequency and width (full width at half maximum, FWHM) of the A$_g$(2) intramolecular mode in the Eu$_{6-x}$A$_x$C$_{60}$ (A = Sr, Ba; x = 0, 3, 5, 6) compounds vs. the unit cell volume. Lattice constants are taken from refs. 1 and 4.
prominent in Sr\(_6\)C\(_{60}\)—in accordance with the stronger hybridization in Sr\(_6\)C\(_{60}\) than Ba\(_6\)C\(_{60}\) due to the smaller lattice constant of the former\(^4\)—and further increases in the Eu containing fullerides.

The band structure of the Eu\(_6\)C\(_{60}\) fulleride has not been studied as of yet, but an enhanced hybridization of the 5\(d\) and/or 6\(s\) orbitals of Eu and the \(t\_1g\) orbital of C\(_{60}\) is plausible owing to its even smaller lattice constant that could explain the larger downshift of the A\(_8\)(2) mode in the Eu-based fullerides. Note that, the electron-phonon coupling for the totally symmetric intramolecular modes of A\(_8\) symmetry is expected to be rather weak—as in the case of metallic alkali fullerides—because of an efficient screening effect.\(^8\) Therefore, the much broader lineshape of the A\(_8\)(2) peak in these systems is also suggestive of significant molecular distortions caused by the stronger hybridization.

Conclusions

Summarizing, Raman spectroscopy suggests considerable structural distortions of the C\(_{60}\) molecular cages in the multinary Eu\(_6\)Sr\(_x\)C\(_{60}\) fullerides with a pronounced metallic character, resulting from their strong interaction with the metal atoms. This can account for the intriguing electronic properties of the studied compounds and the indirect exchange interactions between Eu cations in their ferromagnetically ordered state.

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