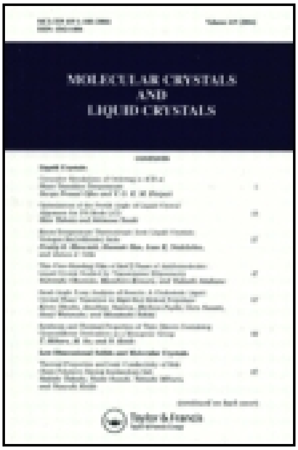

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Crystal Structure of Europium C_{60} Compounds

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Version of record first published: 24 Sep 2006

To cite this article: H. Ootoshi, K. Ishii, A. Fujiwara, T. Watanuki, Y. Matsuoka & H. Suematsu (2000): Crystal Structure of Europium C_{60} Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 340:1, 565-570

To link to this article: http://dx.doi.org/10.1080/10587250008025526

Mol. Cryst. and Liq. Cryst., 2000, Vol. 340, pp. 565-570
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Crystal Structure of Europium C_{60} Compounds

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(Received May 30, 999; In final form July 6, 1999)

We have studied crystal structures of europium C_{60} compounds by high resolution x-ray diffraction measurements. In the systematic synthesis of Eu_xC_{60} for x ($0 \leq x \leq 6$), two stable phases appear at $x = 3$ and 6. Eu_6C_{60} has a *bcc* structure, which is an isostructure to M_6C_{60} (M represents an alkali or alkaline earth metal). Eu_3C_{60} has a superstructure derived by doubling the *fcc* pristine C_{60} crystal along three principal axes. This superstructure comes from an ordering of cation vacancies, which is analogous to $Yb_{2.75}C_{60}$.

Keywords: C_{60}; rare earth fulleride; synchrotron x-ray diffraction

INTRODUCTION

Since the discovery of C_{60} there has been great interest in this novel molecule and many compounds with various atoms and molecules were synthesized. Especially, alkali and alkaline earth fullerides are intensively studied because of the variation of the compounds and superconductivity[1, 2]. Rare earth metals can be good candidates to make compounds with C_{60}, which attract interest not only in superconductivity but also in magnetism originated from localized $4f$ electrons. Superconductivity in rare earth fullerides was reported in $Yb_{2.75}C_{60}$[3] and Sm_xC_{60} ($x \simeq 3$)[4]. As for the Eu compounds, a photoemission study of C_{60} evaporated on Eu revealed the formation of fulleride and the charge transfer from Eu to C_{60}[5]. The bulk compounds of Eu_xC_{60} was synthesized by solid-solid reaction at high temperatures and the compounds of $x = 3$ and 6 were identified[6]. Measurements of their magnetic properties revealed that a magnetic moments was carried by europium ion. However no detailed structural study has not been made so far.

In this paper, we report on the high resolution x-ray diffraction experiments of Eu_xC_{60}. Two stable phases at $x = 3$ and 6 were confirmed in the systematic synthesis of Eu_xC_{60} for $x = 0$ to 6. We also present the crystal structures of these stable phases, Eu_3C_{60} and Eu_6C_{60}.

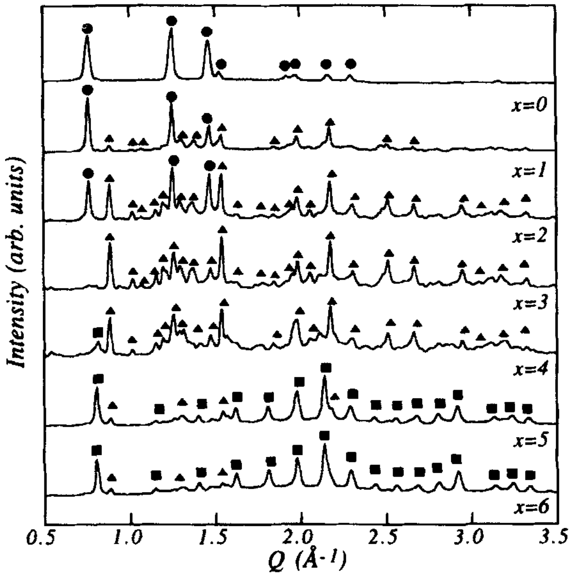

FIGURE 1 X-ray diffraction spectra of Eu_xC_{60} and nominal composition x. Filled circles, triangles, and squares represent main peaks in C_{60}, Eu_3C_{60}, and Eu_6C_{60}, respectively.

EXPERIMENTAL

The polycrystalline samples of Eu_xC_{60} were synthesized by solid state reaction. Stoichiometric mixture of Eu and C_{60} powder was loaded in a tantalum boat and sealed in a quartz tube. Heat treatment was done at 600 °C for about a week. The obtained samples were sealed in a thin glass capillary for x-ray experiments.

Powder x-ray diffraction measurements were carried out by using synchrotron radiation x-rays at Photon Factory (BL-6C_1 and BL-1B), KEK, Tsukuba. The incident x-ray was monochromatized at wavelength 0.6890 Å with a Si(111) double-crystal monochromator. An imaging plate was used for detection of the diffraction, which was converted in the conventional spectrum by integrating the intensity along the Debye ring.

RESULTS AND DISCUSSION

Figure 1 shows the powder x-ray diffraction spectra of Eu_xC_{60} for various

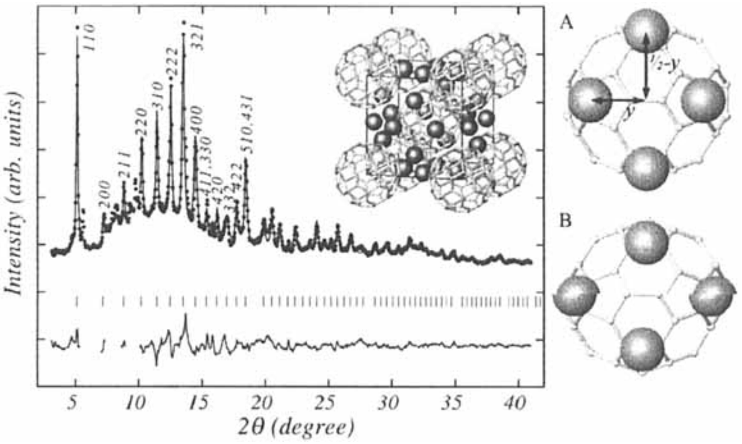

FIGURE 2 Powder x-ray diffraction pattern of Eu_6C_{60} and the result of structural analysis. Dots and solid line represent observed and simulated intensities, respectively. The best R_{wp} is 6.39 %. Some regions at 5-10 degree were excluded in the analysis because of the peaks from a little trace of Eu_3C_{60}. In the excluded region between 5 and 10 degree there is a little trace of Eu_3C_{60}. Inset is the obtained crystal structure of Eu_6C_{60}. Two right figures are views from the [010] direction. A and B correspond two minima of R_{wp} as a function of Eu position y, described in the text.

nominal composition x. The spectra of $x = 1$ and 2 can be understood as a mixed phase of $x = 0$ and 3, while those of $x = 4$ and 5 are considered as a mixed phase of $x = 3$ and 6. We can identify $x = 3$ and 6 as stable phases and no other stable phase exists. This is the same trend as Sm_xC_{60}[7].

Crystal Structure of Eu_6C_{60}

As shown in Fig. 2, almost all peaks in the diffraction spectrum for Eu_6C_{60} can be indexed by a *bcc* lattice with $a_0 = 10.949 \pm 0.007$ Å; the crystal structure is analogous to M_6C_{60} (M is an alkali or alkaline earth metal). The diffraction intensities were analyzed using the RIETAN Rietveld refinement program[8]. In the analysis we removed the region around the peaks which come from a little trace of Eu_3C_{60}. The space group $Im\bar{3}$ was used in accordance with other M_6C_{60}. The C-C bond length of C_{60} is fixed to 1.40 Å for the bond between two hexagons and 1.45 Å for that between hexagon and pentagon. The same temperature factor is assumed for all carbon sites.

TABLE 1 The obtained atomic parameter in Eu_6C_{60}. The space group is $Im\bar{3}$ and the lattice constant is a_0 = 10.949 Å.

Site		x	y	z	B(Å²)
C1	24g	0.0639	0	0.3178	3.4(7)
C2	48h	0.1302	0.1072	0.2769	3.4
C3	48h	0.0662	0.2106	0.2373	3.4
Eu	12e	0.5	0.2763(6)	0	2.9(3)

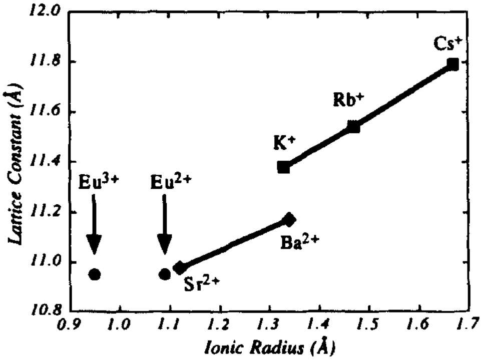

FIGURE 3 Ionic radius v.s. lattice constant in *bcc* M_6C_{60}. Eu_6C_{60} with Eu^{2+} just lies on the divalent line. The lattice constants except for Eu_6C_{60} are quoted from Ref. 9.

Eu atoms are put at 12e $(\frac{1}{2}, y, 0)$ site. Two models for the orientation of C_{60} molecule are considered: One is the ordered model, where all C_{60} molecules are aligned in the same orientation, that is, three orthogonal two-fold axes of C_{60} molecule are parallel to the unit lattice vectors. The other is the merohedral disordered model. The former gives better fit (R_{wp} = 6.39 %) than the latter (R_{wp} = 6.77 %). Orientational ordering of C_{60} is also observed in the alkali and alkaline earth fullerides. On the other hand, we found two minima in R_{wp} as a function of Eu position y, that is, y = 0.2267 (position A, R_{wp} = 6.96 %) and y = 0.2763 (position B, R_{wp} = 6.39 %). The corresponding figures are shown in the right part of Fig. 2. The lower R_{wp} was obtained at the position B, where a cation is attracted toward the hexagon. This result is reasonable because the hexagon is more negatively charged than the pentagon. The obtained atomic parameters are presented in Tab. 1.

Figure 3 shows the relation of lattice constant and ionic radius in *bcc*

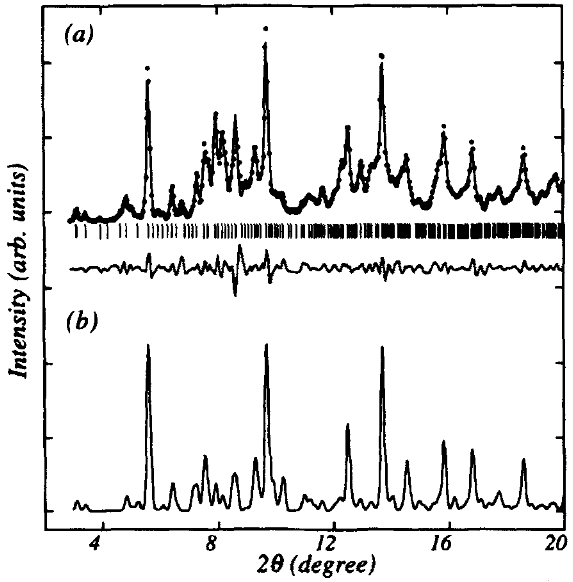

FIGURE 4 (a) X-ray diffraction pattern of Eu_3C_{60}. Dots represent observed points and solid line represents the LeBail fit in $Pa\bar{3}$. (b) Simulated spectrum of $Eu_{2.75}C_{60}$ assuming the same structure as $Yb_{2.75}C_{60}$.

M_6C_{60}, where the case of Eu^{2+} and Eu^{3+} are plotted. If Eu takes divalent state, the lattice constant of Eu_6C_{60} just lies on the extrapolation of Sr_6C_{60} and Ba_6C_{60}. In the case of trivalent Eu ion, the lattice constant should be smaller than the observed value because of smaller ionic radius and stronger Coulomb attraction between Eu and C_{60}. In *bcc* structure of Eu_6C_{60} there is only one crystallographically equivalent site for Eu, so that all cations should have the same magnetic property, namely, a magnetic moment of $7\mu_B$. On the contrary, magnetic measurement[6] showed the coexistence of Eu^{2+} and Eu^{3+}. Curie constant estimated above 150 K can be understood by assuming that half of Eu ions are non-magnetic trivalent state. We can consider some possibilities to explain this inconsistency. One is a static or dynamic reduction of structural symmetry which could not observed in our experiments. Another is that an magnetic interaction between Eu ions, which already exist above 150 K, causes apparently small magnetization.

Crystal Structure of Eu_3C_{60}

Diffraction spectrum of Eu_3C_{60} is shown in Fig. 4(a). We can indexed almost all peaks by the primitive cubic lattice of $a_0 = 28.258 \pm 0.006$ Å, which corresponds the double size of the pristine *fcc* C_{60}. This reminds us of the superstructure of $Yb_{2.75}C_{60}$ type where the cation vacancies in every eight tetrahedral sites are long-range-ordered and ytterbium cations occupy off-centered interstitial sites in the *fcc* C_{60} lattice[3]. LeBail refinement for Eu_3C_{60} was carried out based on the space group $Pa\bar{3}$ and obtained good fit of $R_{wp} = 6.89$ %. The space group of $Yb_{2.75}C_{60}$ is *Pcab* which is a subgroup of $Pa\bar{3}$, but we cannot determined in our experimental condition whether an orthorhombic distortion occurs or not. As shown in the bottom side of Fig. 4(b), we simulated diffraction intensities of $Eu_{2.75}C_{60}$, assuming the same structure as $Yb_{2.75}C_{60}$. It reproduces well the main feature of the observation. The superstructure of Eu_3C_{60} might also originate from the ordering of cation; the model is reasonable to explain such strong intensity of superlattice reflections in the low angle region. However there are somewhat different diffraction intensities between simulation and observation, especially at 6-9 degree, and a more precise structure and stoichiometry analysis should be done.

CONCLUSION

We have studied crystal structures of two europium fullerides, Eu_6C_{60} and Eu_3C_{60} by x-ray diffraction. Eu_6C_{60} has a *bcc* structure with $a_0 = 10.949$ Å, which belongs to M_6C_{60} family of alkali and alkaline earth fullerides. Eu_3C_{60} has a double size of unit cell of pristine C_{60} ($a_0 = 28.258$ Å). This structure is similar to $Yb_{2.75}C_{60}$ and Sm_xC_{60} ($x \simeq 3$), and these Re_xC_{60} with $x \simeq 3$ (Re is a rare earth metal) make a new structural category in fullerene compounds.

Acknowledgments

We wish to thank T. Takenobu and Y. Iwasa for useful suggestions on synthesis. This work was supported by "Research for the Future" of Japan Society for the Promotion of Science (JSPS), Japan. One of the authors, K. I., was supported by JSPS Research Fellowship for Young Scientists.

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