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Magnetic Structure of the Europium Fulleride Ferromagnet Eu_6C_{60}

Irene Margiolaki,[†] Serena Margadonna,*[,‡] Kosmas Prassides,*[,†] Thomas Hansen,[§] Kenji Ishii,[||,⊥] and
Hiroyoshi Suematsu[||,#]

*School of Chemistry, Physics, and Environmental Science, University of Sussex, Brighton BN1 9QJ, U.K.,
Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K., Institut Laue
Langevin, BP 156, 38042 Grenoble, France, and Department of Physics, University of Tokyo,
Bunkyo-ku, Tokyo 113-0033, Japan*

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A remarkable discovery in fullerene chemistry has been the reaction of C_{60} with the strong organic donor tetrakis-dimethyl-amino-ethylene to afford a ferromagnetic (FM) solid, $(TDAE)C_{60}$, with a Curie temperature $T_C = 16$ K.[1] Antiferromagnetic ground states have since been encountered in various fulleride salts, including the polymers RbC_{60}[2] and $Na_2Rb_{0.3}Cs_{0.7}C_{60}$,[3] and the ammoniated salt, $(NH_3)K_3C_{60}$.[4] Despite efforts, no magnetic structure determination has been possible for any of these systems, as no magnetic Bragg scattering has been observed in neutron diffraction experiments, presumably related to the small magnetic moment per C_{60} and the details of the C_{60} magnetic form factor. On the other hand, potentially interesting magnetic molecular materials may be also formed when the metal dopants in fulleride salts carry a magnetic moment. Good candidates are rare-earth fullerides in which the lanthanide ions occupy the interstitial space between the C_{60} units in the solid state, and magnetic correlations involving the unpaired 4f electrons could develop either through direct exchange interactions between the lanthanide 5d−4f orbitals or through π−f interactions modulated by C_{60}. Such an example has been recently provided by work on the phase diagram of Eu-C_{60}, which led to the isolation of the cubic fulleride, Eu_6C_{60}. This displays a transition to a FM state near 14 K which is accompanied by a very large negative magnetoresistance.[5] Here we report a determination of the low-temperature magnetic structure of Eu_6C_{60} by powder neutron diffraction. The configurational symmetry of the magnetic structure is body-centered cubic (bcc), and the magnetic moment per Eu atom refines to 7.1(3) μ_B.

The synchrotron X-ray powder diffraction profile of Eu_6C_{60}[6] at 10 K did not show any reflections violating bcc extinction rules, thus implying the absence of any structural transitions with the crystal structure of Eu_6C_{60} remaining strictly cubic ($a = 10.9286(2)$ Å, space group $Im\bar{3}$, agreement factors of the Rietveld refinement: $R_{wp} = 4.85\%$, $R_{exp} = 8.55\%$, Figure 1S, Supporting Information) to low temperatures, isostructural with Ba_6C_{60}.[7]

To search for scattered intensity of magnetic origin, which provides the unambiguous signature of long-range magnetic order and allows the determination of the spin arrangement, powder neutron diffraction measurements below T_C are necessary. However, natural Eu has an extremely high absorption cross section, σ_a (4530 barns at $\lambda = 1.798$ Å) for neutrons, making such measurements extremely challenging and only possible under carefully optimized experimental conditions.[8] As σ_a is strongly wavelength dependent and shows a minimum at $\lambda = 0.72$ Å,[8] powder neutron diffraction data above (25 K) and below (1.7 K) T_C were collected (22 h runs) on the high-intensity diffractometer D20 at the high-flux reactor at the Institut Laue Langevin (ILL), Grenoble, at $\lambda = 0.808$ Å. The raw data were merged and normalized to standard vanadium runs. At this wavelength, the linear absorption coefficient, μ of Eu_6C_{60}, is 0.948 mm^{-1}. The sample (0.43 g) was introduced in a double-walled vanadium cylinder (5 cm height, 4.5 cm outer diameter, 0.5 mm annular thickness), resulting in a calculated transmission, $T = \exp(-\mu x)$ of 0.39. Appropriate absorption corrections to the neutron data were then applied.[9] Inspection of the 1.7 K diffraction profile revealed a significant increase in the intensities of selected nuclear peaks and the presence of additional reflections of magnetic origin not present at 25 K. The latter could be indexed on the basis of the chemical unit cell (for example, as (310) and (222) in Figure 1), implying that the magnetic and chemical unit cells coincide (magnetic propagation vector, $\kappa = (000)$), as expected for a FM material. In addition, as all reflections obey bcc extinction rules at 1.7 K, the configurational symmetry of the magnetic structure of Eu_6C_{60} is bcc.

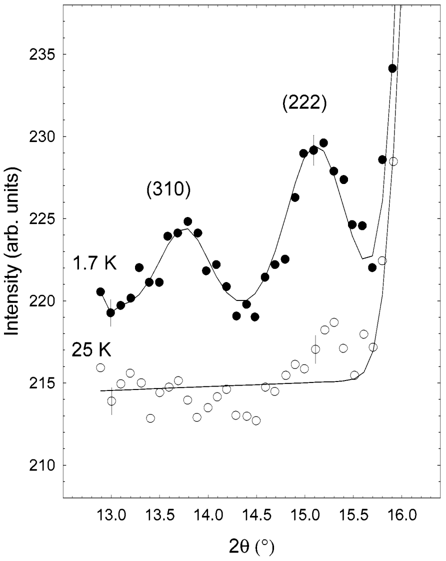

Figure 1. Selected region of the normalized powder neutron diffraction profiles ($\lambda = 0.808$ Å) of Eu_6C_{60} at 1.7 and 25 K showing the appearance of additional reflections below T_C.

Given the paucity of magnetic reflections and the superposition of nuclear and magnetic scattering, the neutron diffraction profile at 25 K was first examined to obtain a starting model for the chemical structure below T_C. Rietveld analysis was initiated with the model obtained from the synchrotron X-ray data. However, the

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* To whom correspondence should be addressed. E-mail: (S.M.) sm413@cam.ac.uk, (K.P.) K.Prassides@susx.ac.uk.
[†] University of Sussex.
[‡] University of Cambridge.
[§] Institut Laue Langevin.
[||] University of Tokyo.
[⊥] Current address: Synchrotron Radiation Research Center, JAERI, Mikazuki-cho, 679-5148 Hyogo, Japan.
[#] Current address: Materials Science Division, JASRI, Mikazuki-cho, 679-5198 Hyogo, Japan.

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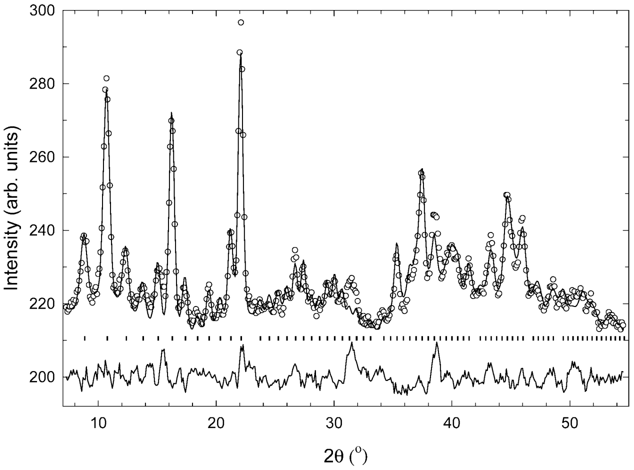

Figure 2. Observed (○) and calculated (−) powder neutron diffraction profile ($\lambda = 0.808$ Å) of Eu_6C_{60} at 1.7 K. The lower line is the difference profile, and the ticks mark the nuclear and magnetic reflections.

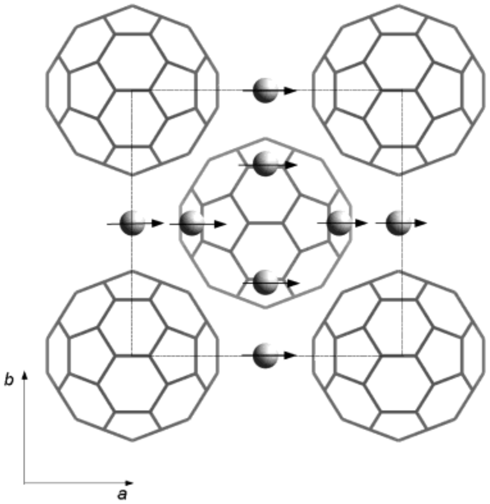

Figure 3. Unit-cell basal plane projection of the crystal and magnetic structure of bcc Eu_6C_{60}. The moment directions are arbitrarily drawn parallel to the *a* axis.

quality of the refinement was unsatisfactory ($R_{wp} = 1.52\%$, $R_{exp} = 0.38\%$). The fit improved significantly when the geometry of the C_{60} units was relaxed and the carbon positions were refined ($a = 10.9292(15)$ Å, $R_{wp} = 1.05\%$, Table 1S, Supporting Information). Rietveld refinement of the neutron diffraction data at 1.7 K was then performed with a two-phase model to account for the chemical and magnetic structures. The former was described with the structural model obtained at 25 K, while for the latter, the magnetic moments of the 12 Eu sites in the unit cell were aligned in the same direction. We note that for a cubic ferromagnet, the spin direction cannot be deduced for randomly oriented domains, as the same magnetic intensities result for any spin direction with respect to the crystallographic axes.[10] The refinement proceeded smoothly resulting in a refined magnetic moment per Eu atom, $\mu = 7.1(3)\ \mu_B$. The final refinement at 1.7 K is shown in Figure 2 ($R_{wp} = 1.08\%$, $R_{exp} = 0.37\%$, $R_{mag} = 14.0\%$, $a = 10.9262(15)$ Å).

Several points arising from the present work are of particular interest. Figure 3 shows a perspective view of the bcc crystal and magnetic structure of Eu_6C_{60}. As the free-ion value of the magnetic moment of Eu^{2+} ($^8S_{7/2}$) is 7.94 μ_B and Eu^{3+} is nonmagnetic ($^7F_0$), the magnetic moment observed at the Eu sites leads to the unambiguous conclusion that Eu is present in the divalent state in Eu_6C_{60}. This is in agreement with field-dependent magnetization measurements at 2 K[5] and contrasts with earlier reports of the presence of sample-dependent Eu mixed valency ($Eu^{2+}/Eu^{3+} \approx 1-4$).[11] Concerning the origin of the FM exchange interactions between Eu^{2+}, we note that the closest $Eu^{2+}-Eu^{2+}$ distance in Eu_6C_{60} is 3.8845(2) Å at 1.7 K, considerably smaller than that in the antiferromagnetic graphite intercalate EuC_6 (∼4.3 Å),[12] but straddling those in FM EuO and EuC_2 (∼3.6−4.1 Å).[13] In the latter, the FM interaction between Eu^{2+} ions is through direct exchange of the nearest neighbor 5d−4f unpaired electrons[13] and T_C scales with the $Eu^{2+}-Eu^{2+}$ distance. However, in Eu_6C_{60}, each Eu^{2+} ion coordinates to two hexagonal and two pentagonal faces of neighboring C_{60} anions and displays short Eu−C contacts: 2.88(1) and 2.90(1) Å to hexagon C(3) and pentagon C(1) atoms, respectively. These are only marginally larger than the sum of the ionic radius of Eu^{2+} (1.12 Å) and the van der Waals radius of C (1.70 Å) and are suggestive of hybridization between the 5d and 6s orbitals of Eu and the t_{1g} orbitals of C_{60}, in analogy with the isostructural and isoelectronic Ba_6C_{60} and Sr_6C_{60}.[7] Such orbital mixing implies that the FM exchange interactions between the 4f electrons are modulated by the $\pi(C_{60})$ orbitals and provides a natural explanation for the conducting and giant magnetoresistive behavior of Eu_6C_{60}.[5]

In summary, we provided the first magnetic structure determination of a fullerene-based molecular ferromagnet by powder neutron diffraction. The lanthanide exchange interactions in Eu_6C_{60} are modulated by the C_{60} anions, and orbital mixing can account for the observed magnetic and conducting properties of the material.

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Supporting Information Available: Rietveld refinement of the synchrotron X-ray diffraction profile and refinement parameters of the neutron diffraction data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Allemand, P.-M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Gruner, G.; Thompson, J. D. *Science* **1991**, *253*, 301.
(2) Chauvet, O.; Oszlanyi, G.; Forro, L.; Stephens, P. W.; Tegze, M.; Faigel, G.; Janossy, A. *Phys. Rev. Lett.* **1994**, *72*, 2721.
(3) Arcon, D.; Prassides, K.; Maniero, A.-L.; Brunel, L. C. *Phys. Rev. Lett.* **2000**, *84*, 562.
(4) Prassides, K.; Margadonna, S.; Arcon, D.; Lappas, A.; Shimoda, H.; Iwasa, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11227.
(5) Ishii, K.; Fujiwara, A.; Suematsu, H.; Kubozono, Y. *Phys. Rev. B* **2002**, *65*, 134431.
(6) The Eu_6C_{60} sample (∼500 mg) was prepared by a solid-state reaction, as described before.[5] High-resolution synchrotron X-ray diffraction data on the sample sealed in a 0.5 mm glass capillary were collected on the BM16 beamline at the European Synchrotron Radiation Facility (ESRF), Grenoble, at 10 K ($\lambda = 0.85044$ Å). Data were rebinned in the range 4−70° to a step of 0.01°. Data analysis was performed with the GSAS suite of powder diffraction programs (Larsen, A. C.; von Dreele, R. B. GSAS software, Los Alamos National Laboratory Report No. LAUR 86-748). In the course of the refinements, the C_{60} anions were in their ideal molecular geometry and were only allowed to dilate radially.
(7) Gogia, B.; Kordatos, K.; Suematsu, H.; Tanigaki, K.; Prassides, K. *Phys. Rev. B* **1998**, *58*, 1077. Saito, S.; Oshiyama, A. *Phys. Rev. Lett.* **1993**, *71*, 121.
(8) Kohlmann, H.; Gingl, F.; Hansen, T.; Yvon, K. *Angew. Chem.* **1999**, *38*, 2029.
(9) Schmidt, D.; Ouladdiaf, B. *J. Appl. Crystallogr.* **1998**, *31*, 620.
(10) Shirane, G. *Acta Crystallogr.* **1959**, *12*, 282.
(11) Ksari-Habiles, Y.; Claves, D.; Chouteau, G.; Touzain, P.; Jeandey, C.; Oddou, J. L.; Stepanov, A. *J. Phys. Chem. Solids* **1997**, *58*, 1771.
(12) Suematsu, H.; Ohmatsu, K.; Yoshizaki, R. *Solid State Commun.* **1981**, *38*, 1103.
(13) Katsuya, T. *IBM J. Res. Dev.* **1970**, *14*, 214.

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