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We report the structural and magnetic properties of the endohedral metallofullerene $Ce@C_{82}$. A hexagonal close packing phase [$P6_3/mmc$ [a=11.1544Å, c=18.2256Å] is formed exclusively after vacuum annealing of the solvent precipitated compound. In contrast, sublimed $Ce@C_{82}$ was found to be dominantly face-centred cubic close packed [Fm-3m; a=15.766Å]. X-ray powder profile calculations revealed that the endohedral cerium atom lies close to 1.8Å from the C_{82} cage centre in both phases. Hexagonal $Ce@C_{82}$ has been investigated by magnetic susceptibility measurements. Paramagnetic behaviour is maintained down to 2K attributable to Ce^{3+} ions. Towards lower temperatures, the observed paramagnetic moment falls from the free ion Ce^{3+}(μ_{eff} =2.54μB) value, monotonically approaching 1μB at 2K.

Keywords: endohedral metallofullerene; $Ce@C_{82}$; polymorphism; magnetism

INTRODUCTION

Endohedral metallofullerenes add a new and interesting branch to fullerene chemistry, having unique structural properties and possibilities of interesting physcial properties. The intrinsically reduced state of the encapsulating fullerene molecule is reminiscent of fullerene intercalation compounds and hence deserves investigation. In this respect, the endohedral lanthanide $Ce@C_{82}$ is an exciting prospect because of the possible co-existence of localized 4f-electrons on cerium and delocalized conduction bands originating from reduced C_{82} [compare with the case of $La@C_{82}$ which shows strong indications of charge transfer to $[La]^{3+}[C_{82}]^{+3}$ [1],[2].

EXPERIMENTAL

Samples of $Ce@C_{82}$ containing soot were obtained *via* an arc discharge method. The $Ce@C_{82}$ was then extracted in solvent, isolated by HPLC[3] and characterised using TOF-Mass spectra and UV-vis-NIR absorption spectroscopies. Crystalline samples of solvated $Ce@C_{82}$ were prepared by slow evaporation from CS_2 solutions. Solvent-free samples were produced *via* two methods: (1) drying under vacuum at 250°C, (2) vacuum sublimation at 600°C. Powder X-ray diffraction experiments were performed at the Photon Factory, KEK, on beam lines BL-1B and BL-6C. Magnetic susceptibility measurements were carried out using a Quantum Design MPMS5 SQUID Magnetometer.

RESULTS AND DISCUSSION

Figure 1a shows the observed profile for vacuum dried $Ce@C_{82}$ (λ=1.6994Å). The profile is single phase and indexes on a hexagonal close packed cell (hcp), space group $P6_3/mmc$ with lattice parameters a=11.1544Å, c=18.2256Å. Calculated hcp $Ce@C_{82}$ profiles were generated using the LAZY-PULVERIX program[4]. In the calculations C_{82} was treated as a hypothetical spherical carbon shell of radius 4.2Å. A series of profiles were calculated as a function of the endohedral cerium atom position within the C_{82} shell. The best comparison of calculated and observed data sets was obtained when the cerium was placed approximately 1.8Å from the C_{82} shell centre (see Figure 1b).

The X-ray profile of sublimed $Ce@C_{82}$ (Figure 2; λ=1.000Å) is biphasic. The dominant phase indexes on a face centred close packed cell (fcc), space group Fm-3m with lattice parameter a=15.766Å. Calculated fcc $Ce@C_{82}$ profiles gave the best comparison to the observed profile when the cerium position was similarly 1.8Å from the cage centre. The minority hcp phase, apparent in the profile as a few broad asymmetric reflections, may result from stacking faulting.

The magnetic susceptibility as a function of temperature (Figure 3a) displays paramagnetism down to 2K. The observed paramagnetic moment is attributed to localised 4f-electrons on the cerium ion (this was inferred by comparison with susceptibility data collected on a sample of hcp $La@C_{82}$)[5]. The temperature dependence of the effective paramagnetic moment μ_{eff} is plotted in Figure 3b. At

300K the effective moment, $\mu_{eff}(300K) = 2.3\mu_B$, is close to the free-ion value for Ce^{3+} (f^1, J=5/2, $\mu_{eff} = 2.54\mu_B$); however, the effective moment decreases towards lower temperatures, reaching $\mu_{eff}(2K) = 1.0\mu_B$.

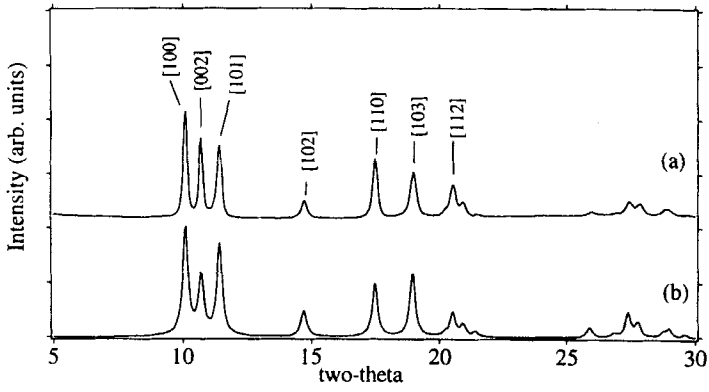

Figure 1: (a) Observed X-ray diffraction profile of dried $Ce@C_{82}$;
(b) Calculated profile of hcp $Ce@C_{82}$; cerium at 1.8Å from shell center.

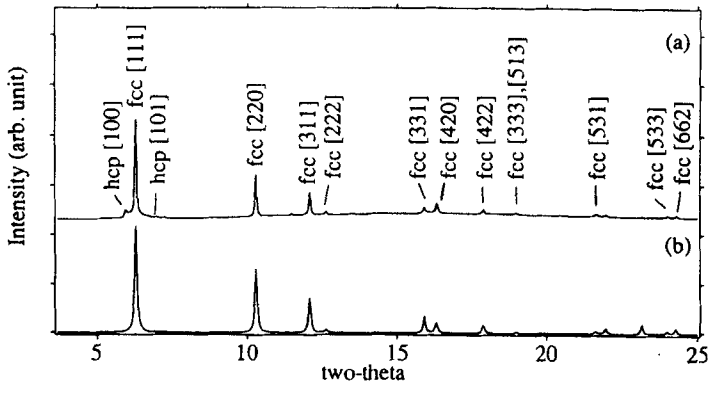

FIGURE 2: (a) Observed X-ray diffraction profile of sublimed $Ce@C_{82}$;
(b) Calculated profile of fcc $Ce@C_{82}$; cerium at 1.8Å from shell center.

One possible explanation for the loss of paramagnetic moment with temperature is that the high temperature disordered cerium atom position becomes quenched upon cooling. This would result in an increase, in the crystal field within the

compound. The ground-state for Ce^{3+} (J=5/2) is expected to be $|J_Z|=1/2$ giving a $\mu_{eff}(0K) = 0.74\mu_B$, close to the observed value at 2K.

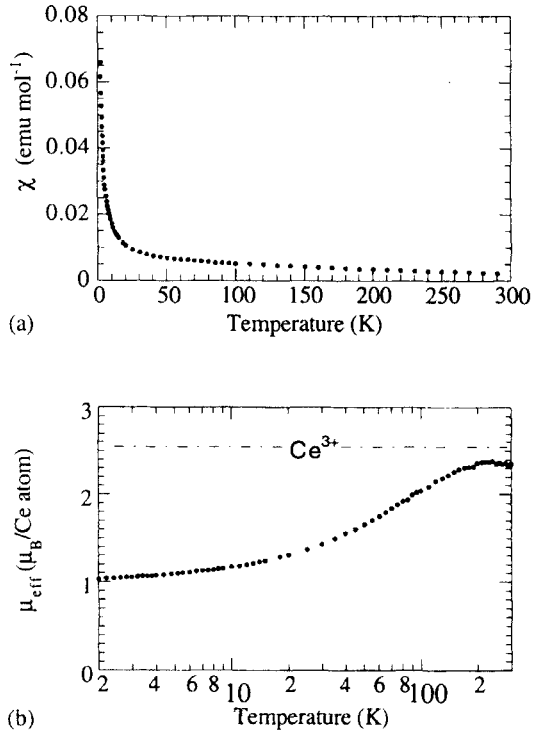

FIGURE 3: (a) Susceptibility (χmol^{-1}) behaviour of $Ce@C_{82}$ versus temperature and (b) Plot of μ_{eff} of $Ce@C_{82}$ versus temperature.

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