ESRF	**Experiment title:** Crystal structures of lanthanide fullerides - remarkable giant lattice response	**Experiment number**: CH-1626
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Report:

Abstract of publication resulting from this proposal:

Temperature-induced valence transition and associated lattice collapse in samarium fulleride, *Nature* 2003, *425*, 599-602.

The different degrees of freedom of a given system are usually independent of each other but can in some materials be strongly coupled, giving rise to phase equilibria sensitively susceptible to external perturbations. Such systems often exhibit unusual physical properties that are difficult to treat theoretically, as exemplified by strongly correlated electron systems such as intermediate-valence rare-earth heavy fermions and Kondo insulators, colossal magnetoresistive manganites and high-transition temperature (high-T_c) copper oxide superconductors. Metal fulleride salts—metal intercalation compounds of C_{60}—and materials based on rare-earth metals also exhibit strong electronic correlations. Rare-earth fullerides thus constitute a particularly intriguing system—they contain highly correlated cation (rare-earth) and anion (C_{60}) sublattices. Here we show, using high-resolution synchrotron X-ray diffraction and magnetic susceptibility measurements, that cooling the rare-earth fulleride $Sm_{2.75}C_{60}$ induces an isosymmetric phase transition near 32 K, accompanied by a dramatic isotropic volume increase and a samarium valence transition from (2+ε)+ to nearly 2+. The negative thermal expansion—heating from 4.2 to 32 K leads

to contraction rather than expansion—occurs at a rate about 40 times larger than in ternary metal oxides typically exhibiting such behaviour. We attribute the large negative thermal expansion, unprecedented in fullerene or other molecular systems, to a quasi-continuous valence transition from Sm^{2+} towards the smaller $Sm^{(2+\varepsilon)+}$, analogous to the valence or configuration transitions encountered in intermediate-valence Kondo insulators like SmS.

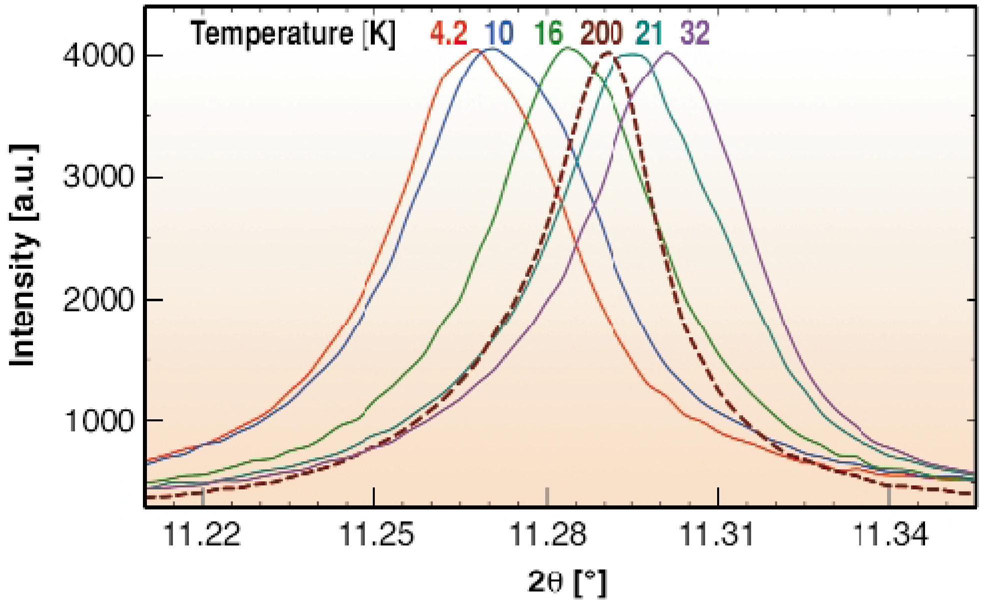

Figure 1 Selected region of the diffraction profile of $Sm_{2.75}C_{60}$ showing the temperature evolution of the (444) Bragg reflection (λ = 0.79980 Å).

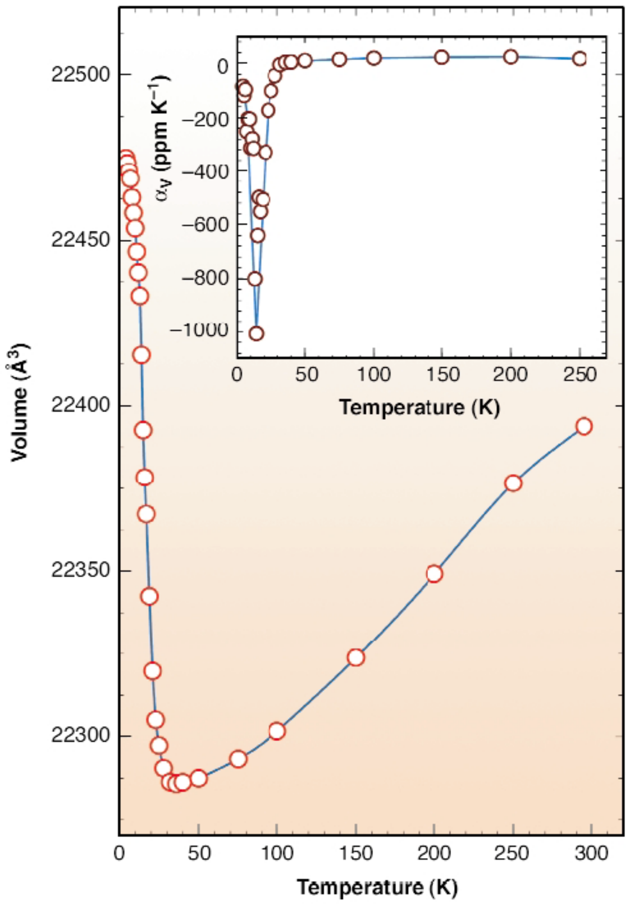

Figure 2. Temperature evolution of the orthorhombic unit cell volume of $Sm_{2.75}C_{60}$. The inset shows the temperature dependence of the coefficient of thermal expansion, $\alpha_V = d\ln V/dT$.