The properties displayed by the series of ammoniated fullerides, \((\text{NH}_3)_x\text{Na}_2\text{C}_{60}\) (0.5 ≤ \(x\) ≤ 1, \(A=\text{K}, \text{Rb}\)) have been quite puzzling. In these systems, the \(fcc\) structure is maintained with the ammonia coordinated to the sodium ions and the \(\text{Na}^+-\text{NH}_3\) pairs residing in the octahedral sites. However, the \(T_c\)s are dramatically lower than expected and, in addition, they decrease with increasing lattice constant, showing a trend which is completely different from the conventional one.

Suppression of superconductivity was associated with the presence of \(\text{Na}^+\) ions displaced from the center of the octahedral sites which leads to a non-cubic local potential on \(\text{C}_{60}^-\) and could lift the triple degeneracy of the \(t_{1u}\) LUMO.

In an attempt to obtain a better understanding of the structure of these ammoniated fullerides and its implications for superconductivity, we have undertaken a systematic combined high resolution synchrotron X-ray and neutron diffraction study of the series of perdeuterated superconductors, \((\text{ND}_3)_x\text{NaKRB}_{2}\text{C}_{60}\) and \((\text{ND}_3)_x\text{NaRbC}_{60}\) (0.7 ≤ \(x\) ≤ 1). By combining the complementary advantages of the two techniques, we have been able to monitor the structural properties as a function of ND content, \(x\) and determine the exact stoichiometric compositions and the geometry of the \(\text{Na}^+-\text{ND}_3\) pairs, factors which alter the local potential on the \(\text{C}_{60}\) units and/or the electronic states. We find that the displacement of the \(\text{Na}^+\) ions from the center of the octahedral interstices is much larger than reported before (in excess of 2.0 Å).