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**ESI\_Fig. 1:** Plot of the (representative) standard uncertainties on the extracted H1/D1 parameters (normalised to the s.u. on the longest data set) vs. cumulative counting times for  $SrH_2$  and  $SrD_2$ .

Data had been collected originally as a series of 5 min accumulations from samples of polycrystalline  $SrH_2$  and  $SrD_2$  at 2 K. The diffraction patterns were summed into cumulative sets after each 5 min interval to produce data sets of varying collection times, which were then used to refine the structural models. Plots of the refined scale factor *vs*. the cumulative counting time resulted in a linear relationship, demonstrating the stability of the detectors with respect to the high number of counts over time. The parameters allowed to vary were the atom positions, isotropic ADPs, the scale factor and the background terms. The zero parameter and the peak shape parameters were assumed to remain constant throughout the data collection, so were refined against the longest data collection (120 min for  $SrH_2$ , 30 mins for  $SrD_2$ ) and consequently fixed for the sequential refinement of the shorter data sets. The structures were refined using no constraints on either bond lengths or angles.

A plot of the s.u's for the H1 x coordinate for both  $SrH_2$  and  $SrD_2$  normalised to the s.u. of the data set with the longest counting time (see ESI\_Figure 1) showed that the standard uncertainties decrease with increased counting time until they reach a minimum and thereafter remain almost constant (a trend which is representative of the standard uncertainties for the other extracted parameters). After a certain optimum counting time, the s.u's can be attributed to systematic errors associated with the instrument and experimental set-up, and counting in excess of this optimum time results in no further improvement in the precision of the extracted parameter. This occurred for the  $SrD_2$  compound at approximately 30 mins; the corresponding saturation time for the  $SrH_2$  compound was approximately 90 mins.



**ESI\_Fig. 2:** Refined values for a)  $(SrH_2)$  H1 x coordinates and b)  $(SrD_2)$  D1 x coordinates and c)  $(SrH_2)$  H1 isotropic atomic displacement parameters and d)  $(SrD_2)$  D1 isotropic ADPs, plotted against collection time (mins) on the x axis.

Plots of the evolution of selected extracted parameters with cumulative counting times (see ESI\_Figure 2) demonstrate the s.u. values on the refined H1/D1 x coordinate and the H1/D1 Uiso value with collection time. The s.u. values for the hydrogenous sample (ranging from 2.7 x  $10^{-4} - 1.1 \times 10^{-3}$  for the longest data set) were larger than for the deuterated (ranging from  $1.0 \times 10^{-4} - 2.4 \times 10^{-4}$  for the longest data set) and probably reflected the former's lower peak-to-background ratios.

Plots of the H1/D1 x coordinate vs. collection time show that although the s.u's are larger for the 5 min data collection, the value of x refined from the 5 min data set is in good agreement with (being well within the s.u. range of) the value refined from the longest (120 min for SrH<sub>2</sub>, 30 mins for SrD<sub>2</sub>) data set. (The value of the H1 Uiso refined from the 5 min data set, however, was slightly above the upper limit of the s.u. of the value refined from the 90 min data set, indicating that data collections of at least 15 mins would be needed to extract accurate values for the Uiso's of the hydrogenous compound.)



**ESI\_Fig. 3:** Profile fit to the raw 2 K neutron powder diffraction data (range  $20^{\circ}$  to  $145^{\circ} 2\theta$ ) for SrH<sub>2</sub> and (b) the data after background subtraction using a 30-parameter Chebychev polynomial. Note that the (101) peak (visible only as a Bragg marker on the far left of the top profile) was of negligible intensity, so was excluded to allow a better fit to the background.



**ESI\_Fig. 4**: (a) Background-subtracted refined profile fit for  $BaH_2$  at 2 K (120 min collection), showing the experimental data points, the profile fit and the difference plot, below. The upper row of tick marks relate to the peak positions of the BaO impurity phase. (b) The corresponding 2 K profile fit for  $BaD_2$  (30 min collection).



**ESI\_Fig. 5**: A comparison of the H/D environments (refined with isotropic thermals) from 2K NPD data of BaH2/D2: (a) H1; (b) H2; (c) D1 and (d) D2.

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**ESI\_Fig. 6:** Comparative plots of the evolution of a) Sr x fractional coordinate, b) Sr z fractional coordinate, c) H1/D1 x fractional coordinate, d) H1/D1 z fractional coordinate; e) H2/D2 x fractional coordinate and f) H2/D2 z fractional coordinate; g) H1/D1 isotropic ADP and h) H2/D2 isotropic ADP with temperature. The x axis in each case is temperature in K. Extracted parameters refined from the SrH<sub>2</sub> data are shown as white triangles, SrD<sub>2</sub> are black circles.

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**ESI\_Fig. 7:** Comparative plots of the evolution of a) Ba x fractional coordinate; b) Ba z fractional coordinate c) H1/D1 x fractional coordinate; d) H1/D1 z fractional coordinate; e) H2/D2 x fractional coordinate; f) H2/D2 z fractional coordinate; g) H1/D1 isotropic ADP and h) H2/D2 isotropic ADP with temperature. The x axis in each case is temperature in K. Extracted parameters refined from the BaH<sub>2</sub> data are shown as white triangles, BaD<sub>2</sub> are black circles.



**ESI\_Figure 8:** Comparison of the normalised lattice parameter expansion in  $SrH_2$  and  $SrD_2$  with temperature, showing more rapid expansion for the deuteride along each axis, where  $a_o$ ,  $b_o$  and  $c_o$  refer to the lattice parameters at 2 K.