Disorder in Rare Earth Metal Halide Carbide Nitrides

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Structural frustration in a rod packing exhibits analogy to frustration effects in antiferromagnetic systems. Like the spins in a triangular Ising net, rods with periodic contour may arrange randomly. Such frustration effects are observed in rare earth metal carbide nitride halides composed of C_2 centered RE_6 octahedra and N centered RE_4 tetrahedra. These can be connected in varying sequences to form infinite rods or fragments of rods. Two types of rods are essential which are depicted in Fig. 1. The first is composed of alternating single octahedra and double tetrahedra $^1_\infty$[ott]. They are aligned in a parallel fashion in the structure of β-Gd_4I_6CN to form a Kagomé-type arrangement of triangles and hexagons with additional rods centering the hexagonal channels. Every third rod of the latter type is rotationally disordered. The other type of rod formed from alternating double octahedra and double tetrahedra $^1_\infty$[oott] occurs in phases characterized as $Y_6I_9C_2N$. We show structural variants which exhibit different degrees of disorder on micro- and nanoscale.

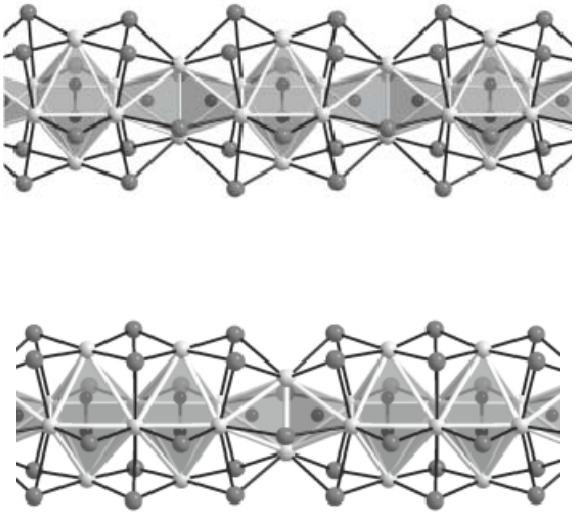

Figure 1: Side view of (top) a rod $(C_2)(N)_2Ce_8I_6$, notation $^1_\infty$[ott] and (bottom) $(C_2)_2(N)_2C_{12}I_{18}$, notation $^1_\infty$[oott].

The hexagonal structures of the phases with compositions $Ce_6I_9C_2N$ and Ce_4I_6CN, respectively, are closely related in their metrics and mainly differ by a stepwise change of disorder. The common feature of the structures is the Kagomé-type pattern depicted in figure 2. It seems to be identical in the projection along [001] although the constituents are different, namely $^1_\infty$[ott]-type rods in the structure of Ce_4I_6CN and $^1_\infty$[oott]-type rods in the case of $Ce_6I_9C_2N$. The rods are connected via iodine bridges. The atomic positions with respect to the *c* axis are identical for different rods, and the connections are exclusively between one octahedron apex and the waist of an octahedron in an adjacent rod.

The question arises what causes the different degrees of disorder in the phases discussed. (i) The distances in the Ce-I-Ce bridges within the Kagomé-type framework are approximately 0.3 Å shorter than those involving the rods inserted into the hexagonal channels. Hence, the comparably weaker bonding favors rotational disorder. (ii) There exists a triangular arrangement of contoured rods with minima and maxima in diameter at identical height along *c* for all of them. A close packing of such rods can be optimized by mutually shifting them along *c* with a positional ratio 1:2 in each triangle. Such a condition corresponds to maximal frustration and obviously partly occurs as indicated by the results of structure refinement and the significant excess electron densities observed. (iii) The first coordination shell, the hexagonal channel, for all inserted rods is identical, no matter whether there is order or disorder. However, provided the channel adjusts marginally to the respective rod orientation,

then interaction within the triangular arrangement is possible, and the second coordination shell becomes important. (iv) Indeed, sketches of the ordering patterns presented in figure 3 give evidence for an influence via the symmetry of the second coordination shells in the structures of β´- and ß´´-$Ce_6I_9C_2N$ as well as Ce_4I_6CN. Figure 3 also presents a hypothetical case of total order for all rods inserted into the Kagomé-type framework.

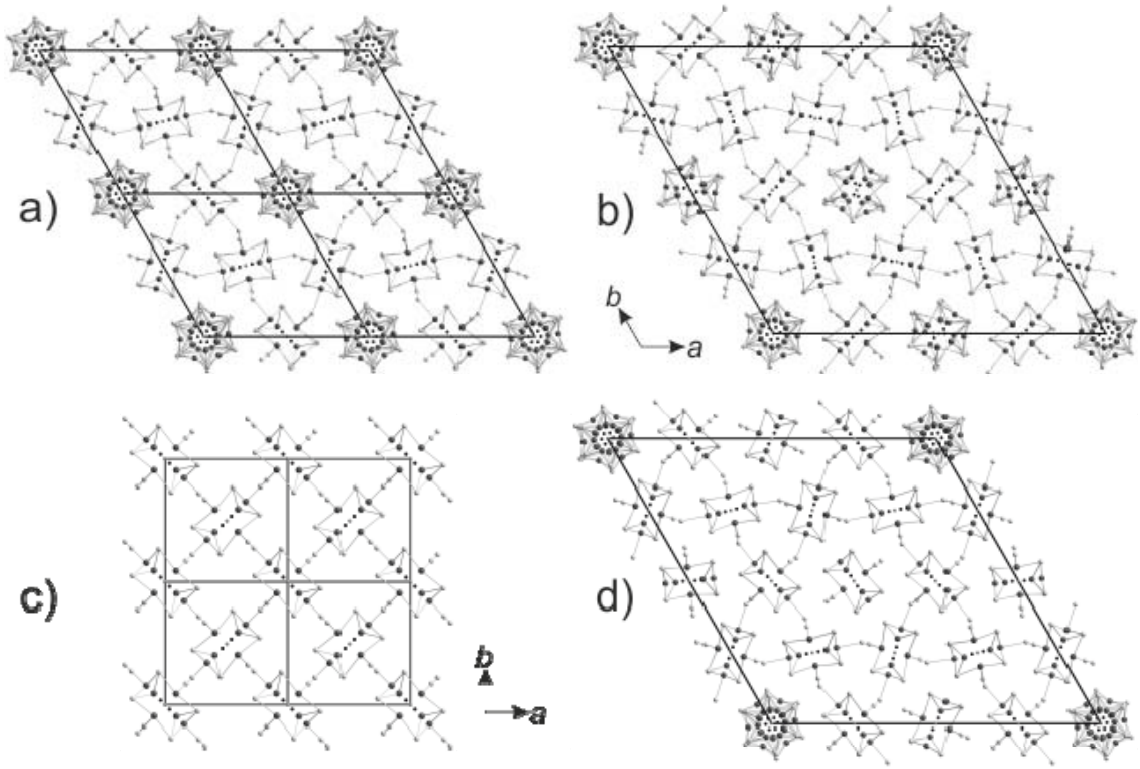

Figure 2: Projections along [001] of (a) ß´´-$Ce_6I_9C_2N$, (b) β´-$Ce_6I_9C_2N$, (c) Ce_4I_6CN and (d) β-Gd_4I_6CN.

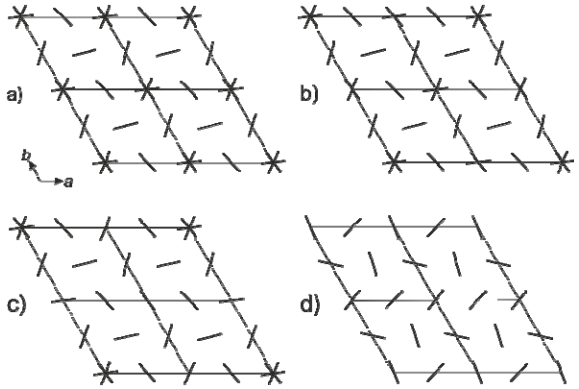

Figure 3: Schematic disorder patterns of the structures of (a) ß´´-$Ce_6I_9C_2N$, (b) β´-$Ce_6I_9C_2N$, (c) β-Gd_4I_6CN and (d) $RE_6I_9C_2N$ hypothetical, ordered.