

Liquid-solid directional composites and anisotropic dipolar phases of polar nanoregions in disordered perovskite: supporting information

Jacopo Parravicini,^{1,*} Eugenio DelRe,² Aharon J. Agranat,³ and Gianbattista Parravicini⁴

¹*Material Science Department, Università di Milano-Bicocca, 20125 Milano, Italy*

²*Physics Department, "Sapienza" Università di Roma, 00185 Roma, Italy*

³*Applied Physics Department, Hebrew University of Jerusalem, 91904 Israel*

⁴*Physics Department, Università di Pavia, 27100 Pavia, Italy*

EIGHT SITES MODEL IN PEROVSKITES

When a crystalline ABO_3 perovskite structure is considered, the amount of the disorder is associated to the different occupation probabilities of the B -cation for 8 energetically equivalent sites positioned along the diagonals of the conventional perovskite cubic cell [1–3], as depicted by the scheme in Fig. 1.

In this arrangement, the allowed directions depend on the long-range-symmetry crystalline phase: in the lowest-temperature *rhombohedral phase* there is just one position of the B -cation with the greatest occupation probability (Fig. 1(a)); in the *orthorhombic phase* two equally probable B -cation positions can be found (Fig. 1(b)); in the *tetragonal phase* there are four equivalent highest occupation probability positions (Fig. 1(c)); in the *cubic phase* the B -cations can be displaced with the same probability along all directions of the 8 sites, i.e. all directions are disordered (Fig. 1(d)). Therefore, this microscopic pattern predicts 12 order-disorder states combinations

*Corresponding author: jacopo.parravicini@unimib.it

with respect to the considered phase and crystalline direction (see Fig. 2), with three directions ordered in the *rhombohedral phase* ("ooo"; solid, solid, solid), two directions ordered and one disordered in the *orthorhombic phase* ("ood"; solid, solid, liquid), two directions disordered and one ordered in the *tetragonal phase* ("odd"; solid, liquid, liquid), and three directions disordered in the *cubic phase* ("ddd"; liquid, liquid, liquid).

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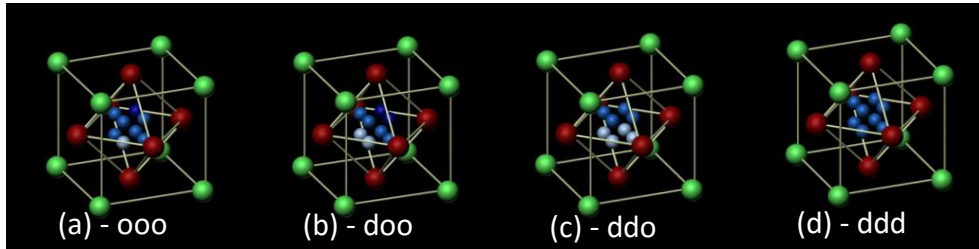


FIG. 1: Scheme of the order/disorder microscopic phase transitions allowed by the model of Comès et al. [1, 2] for our case, with the O ions (red), K/Na ions (A anions, green), and Ta/Nb ions (B cations, blue) exhibiting jumps between eight off-center energetically equivalent positions: shades of blue from bright to dark illustrate occupancy probabilities from most to less probable for nominally (a) rhombohedral (three direction ordered, “ooo”), (b) orthorhombic (two directions ordered, “doo”), (c) tetragonal (two directions disordered, “ddo”), (d) cubic (three directions disordered, “ddd”). This very same order-disorder sequence is found to hold also for the KNTN macroscopic response (see Fig. 2 of main text).

| Crystalline phase Crystal-line direction | Rhombic hedral | Ortho rhombic | Tetra gonal | Cubic |
|---|-------------------|------------------|----------------|------------|
| (a) | ordered | disordered | disordered | disordered |
| (b) | ordered | ordered | disordered | disordered |
| (c) | ordered | ordered | ordered | disordered |

FIG. 2: Scheme of the 12 order/disorder combinations, as a function of the crystalline directions and the long-range symmetry phases, allowed by the model of Comès et al. [1, 2].