Prussian blue analogues (PBA) form a family of materials that are used as prototype of porous solids for hydrogen storage. Their porous framework is related to systematically arranged vacancies in the building block, \([\text{Mn(CN)}_6]^{\text{n-6}}\). The accepted structural model for these materials (cubic) assumes a random vacancy distribution, which results in a 33% of framework free volume. Nevertheless, recent spectroscopic and structural evidences show that such a model is a limiting case. Vacancies remain ordered or at least partially ordered and thus another structural model needs to be considered i.e., a model (also cubic). In such a model, the accessible framework volume reaches 50%. For copper PBA, conclusive evidence on an ordered vacancies system has been obtained and the hydrogen storage capacity for this material is the highest within the series \([1]\). High-resolution electron microscopy (HREM) appears as an excellent tool to shed light on the vacancy distribution in PBA and related solids. The TEAM 05 microscope is used at 80KV. Focal series are used to apply the exit wave reconstruction (EWR) procedure and obtain phase and amplitude images from low dose experimental images. This is done in order to minimize beam sample interaction. As reference material, the rhombohedral phase of the Zn analogue is used where the porous framework is not related to the existence of vacant sites. Figure 1 shows a nanoparticle of Cu containing PBA material. The particle has different crystalline regions that are enlarged in Fig. 1b-c together with some FFT spectra. The dose rate in use is 200 e/Å²s. Ordered vacancies are very apparent in this structure (see arrows). The basic cubic structure can be also seen according to the different projections in the powder particle. For instance, Figs. 1b-c show a projection along [011] although each blob is formed by a number of intensity maxima. This is most likely the center of charge in the structure formed by light atoms (C and N, mainly). Fig. 1c shows a grain boundary and also details of the center of charge in the structure. Fig. 2a shows a view of the Zn containing PBA material at a dose rate of 420 e/Å²s. Figs. 2b-d show phase images of the same area but with a reduced dose of 115 e/Å²s. These phase images show details of the atomic arrangement and the center of charge as well. In addition, they suggest rather small cavities or arrangements of vacancies in a disordered manner. Starting from the nanopore apparently two layers with different Z position overlap producing a slight displacement in X,Y directions and give rise to the image when the projection is considered. The obtained results are conclusive on the presence of a system of ordered vacancies for copper PBA.

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Fig. 1: (a) Cu rich PBA material powder nanoparticle imaged with an electron dose rate of 200 e/Å²·s. (b-c) enlargement of selected areas in (a) and corresponding FFTs.

Fig. 2: (a) Zn containing PBA material at a dose rate of 420 e/Å²·s. (b,c) Phase images (40 image focal series at a dose rate of 115 e/Å²·s) after EWR around a nanopore in the Zn containing PBA material and corresponding FFTs.