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Imaging LiBC by phase-contrast scanning transmission electron microscopy

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The visualization of light elements is a particular challenge for electron microscopy as the contrast in most methods strongly depends on the scattering potential of the specimen. Although it was found possible to estimate Li in $LiCoO_2$ by HRTEM [1], recently scanning transmission electron microscopy (STEM) bright field methods have produced more promising results. In particular, annular bright field STEM is utilized for such investigations, e.g. for detecting Li in battery materials [2]. Phase-contrast STEM also is a suitable tool for the detection of light element positions, as demonstrated e.g. for O in $SrTiO_3$ [3]. Thus, we evaluated this method for the investigation of LiBC, an interesting compound in different aspects consisting of light elements only. Phase-contrast STEM (PC-STEM) imaging [4,5] represents an increasingly important alternative to the well-established HRTEM method. The image contrast in both methods is coherently generated and thus depends not only on illumination and collection angles but on defocus and specimen thickness as well.

Hexagonal platelets of LiBC were synthesized from the elements by heating at 1523 K in inert atmosphere [6]. Boron and carbon form planar hetero graphite layers of the isoelectronic hexagonal BN type. These BC six-ring layers are stacked ecliptically such that B and C alternate along the *c* axis. Li is intercalated between these layers ($P6_3/mmc$; a = 275.2 pm; c = 705.8 pm) [6]. The STEM investigations were performed on a dedicated STEM microscope (Hitachi HD-2700CS with cold-field emitter, V_{acc} = 200 kV). An aberration-corrector (CEOS) optimizes the performance of the probe-forming objective lens resulting in a resolution better than 0.1 nm [7]. In the phase contrast mode, a variant of the bright field (BF) STEM method using a small BF detector, mainly diffracted beams contribute to the image. Image simulations were performed by multi-slice calculations with the EMS program [8] taking the parameters of the microscope and the crystallographic data of LiBC [6] into account.

The hexagonal structure of LiBC was investigated in projection along the *c* axis. For this, the orientation of the selected crystal area was adjusted in the nano diffraction mode (Figure 2a). The focus dependency of PC-STEM imaging is demonstrated in Figure 1 where a contrast inversion is observed. Higher magnified images recorded at a small defocus value reveal an arrangement of rings of six bright spots that are mostly centered by a fainter spot (Figure 2b,c). The comparison with simulated images allowed us to assign the bright spots to the positions of the B and C atoms while the faint central spot corresponds to the Li position (Figure 2d). Defects in the BC substructure have not been observed, but there are frequent positions in the center of the BC hexagons that are obviously not occupied by Li atoms as they appear dark (Figure 2c). Its semiconducting behavior makes it less likely that empty Li positions are an intrinsic property of the LiBC structure but may be induced by the measurement: the enhanced mobility of Li^+ might be caused by the electron beam. In NMR studies, Li mobility was found to be very small up to 500 K [9]. As the LiBC structure is slowly destroyed during the measurement and is finally getting amorphous after a few minutes, vacancy formation is most likely due to the action of the electron beam (Figure 1b) [10].

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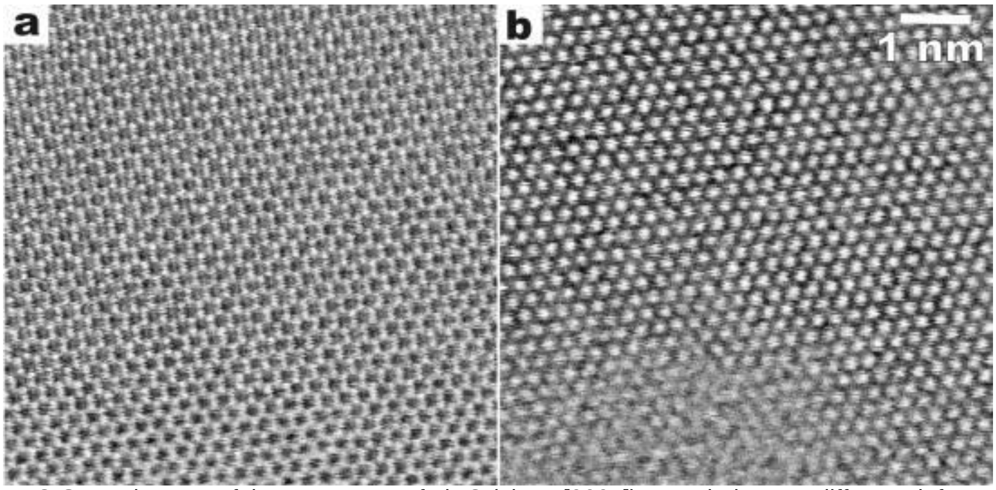

Figure 1. PC-STEM images of the same area of LiBC (along [0001]) recorded at two different defocus values *f* ($\Delta f \approx 20$ nm) show a contrast inversion. The lower left part in (b) is already affected by amorphization of the structure in the electron beam.

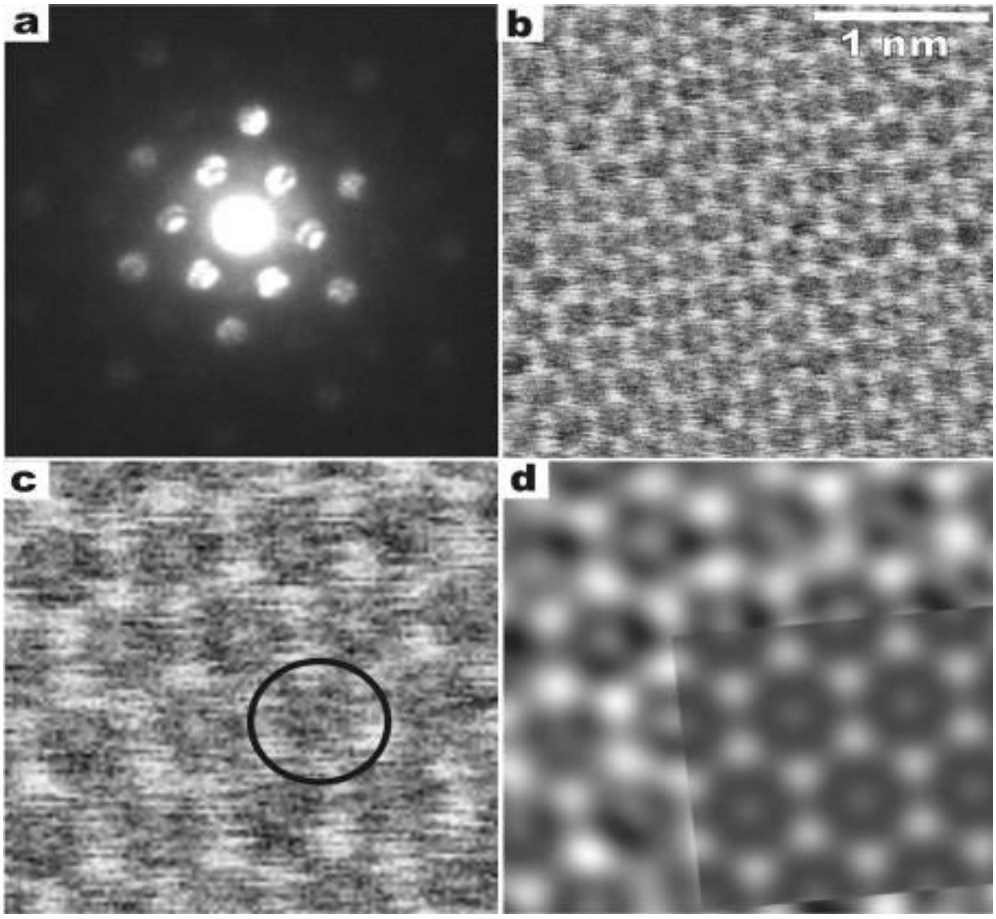

Figure 2. LiBC along [0001]. (a) Nanodiffraction pattern. (b) PC-STEM image as obtained. (c) Magnified section of (b). The circle marks an empty Li position. (d) Fourier filtered image (c) with a simulation fitted in. The simulation was calculated using the multi-slice algorithm of the EMS program for a defocus of $f = 5$ nm and a thickness of 5.6 nm [7]. Microscope parameters: $V_{acc} = 200$ kV; $C_s = 10$ μm; $C_c = 1.6$ mm; variation of $\Delta f = 5$ nm, reciprocal diameter of the objective aperture $D^{-1} = 25.4$ nm^{-1}; beam semi convergence = 1.5 mrad.