Crystal structures of superconducting sodium intercalates of hafnium nitride chloride

J. Oró-Solé [a], C. Frontera [a], D. Beltrán-Porter [b], O.I. Lebedev [c], G. Van Tendeloo [c], A. Fuertes [a,*]

[a] Institut de Ciència de Materials de Barcelona (CSIC), Campus UAB, 08193 Bellaterra, Spain
[b] Institut de Ciència de Materials de la Universitat de València, PO Box 2085, Polígono "La Coma" s/n, 46980 Paterna, Spain
[c] EMAT, RUCA, Groenenborgerlaan 171, Antwerp 2020, Belgium

Dedicated to Professor Gérard Férey on the occasion of his 65th birthday.

Abstract

Sodium intercalation compounds of HfNCl have been prepared at room temperature in naphtyl sodium solutions in tetrahydrofuran and their crystal structure has been investigated by Rietveld refinement using X-ray powder diffraction data and high-resolution electron microscopy. The structure of two intercalates with space group $R\bar{3}m$ and lattice parameters $a = 3.58131(6)$ Å, $c = 57.752(6)$ Å, and $a = 3.58791(8)$ Å, $c = 29.6785(17)$ Å is reported, corresponding to the stages 2 and 1, respectively, of Na_xHfNCl. For the stage 2 phase an ordered model is presented, showing two crystallographically independent [HfNCl] units with an alternation of the Hf–Hf interlayer distance along the c-axis, according with the occupation by sodium atoms of one out of two van der Waals gaps. Both stages 1 and 2 phases are superconducting with critical temperatures between 20 and 24 K, they coexist in different samples with proportions depending on the synthesis conditions, and show a variation in c spacing that can be correlated with the sodium stoichiometry. High-resolution electron microscopy images of the host and intercalated samples show bending of the HfNCl bilayers as well as stacking faults in some regions, which coexist in the same crystal with ordered domains.

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1. Introduction

The layered compounds β-MNX (M = Hf, Zr; X = Cl, Br) crystallize in the rhombohedral SmSI structure with space group $R\bar{3}m$ [1–3]. They may be described as nitride interstitial derivatives of ZrCl, preserving the space group and similar coordinates for metal and halide atoms [4]. The intercalated compounds M_xZrNCl, M_xZrNBr and M_xHfNCl (M = alkaline metal) are d^1/d^0 iono-covalent superconductors with some of the highest critical temperatures

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observed for inorganic non-oxide materials [5–7]. For sodium intercalated hafnium nitride chloride a superconducting phase has been reported with critical temperatures of 20, 23 or 24 K [8–11] and in lithium intercalated HfNCl, critical temperatures of 18, 20, 24 and 26 K [5,12,13] have been observed in different samples showing in some cases co-intercalated organic molecules. In both systems as well as in doped zirconium nitride chloride with T_c = 12 K, the influence on the superconducting properties of factors such as the nature of the transition metal, the co-intercalated molecules and the doping level are still not yet completely understood. The crystal structure of $Na_{0.29}HfNCl$ has been reported as isotypic to YOF with space group $R\bar{3}m$ and crystal parameters a = 3.5892(3) Å and c = 29.722(3) Å [8]. The interlayer spacing is 1/3 of the c parameter, being 9.80 Å for $Na_{0.29}HfNCl$ and 9.22 Å for the pristine, β-HfNCl [1]. Staging during intercalation of the layered compounds is a phenomenon that has been frequently observed in graphite and in transition metal dichalcogenides, in which a unit consisting of a guest layer followed by n host layers (for a stage-n compound) is repeated along the c axis [14–16]. The phase with composition $Na_{0.29}HfNCl$ can be described as a diluted stage 1 intercalate, with all the van der Waals gaps partially filled with sodium atoms. In a recent paper we reported a new intercalated phase in this system, showing interlayer separations between 9.48 and 9.67 Å, which is obtained as an intermediate in the intercalation process of the host to give the previously reported phase with composition $Na_{0.29}HfNCl$. The new sodium intercalated compounds were prepared at room temperature, by treatment of the host with naphtylsodium solutions in tetrahydrofuran. The intermediate phase shows a critical temperature of 20 K and can be interpreted as a second stage intercalate of HfNCl [17]. The use of high resolution powder X-ray diffraction allowed us to show that all the samples contain more than one phase, being most frequently biphasic, with the host, the stage 1 and the stage 2 coexisting in different proportions. In this paper we present a comparative study of the crystal structure of the new stage 2 phase and a stage 1 phase coexisting in the same sample, through Rietveld refinement using high-resolution X-ray powder diffraction data. We also report the first high-resolution electron microscopy study for the superconducting intercalated samples.

2. Experimental

HfNCl was prepared from hafnium (Aldrich 99.5%) and ammonium chloride (Aldrich 99.99%) in the stoichiometric ratio 1:1.1, treated at temperatures between 740 and 780 °C for 12 h in sealed evacuated silica tubes (length: 25 cm, inner diameter: 8 mm). In a second step a temperature gradient of 100 °C was applied to the same reaction tube and the sample was recrystallized by chemical vapour transport. Sodium intercalation reactions were performed by the treatment of recrystallized HfNCl with naphtyl-sodium solutions in tetrahydrofuran prepared by reaction of naphthalene and metallic sodium in concentration 1 M. The intercalation reaction time was 24 h and the molar ratio Na:HfNCl was 52:1. Filling of the reaction tubes as well as intercalation reactions and handling of the products for subsequent characterization were performed in a glove box under re-circulating argon. Sodium analyses were performed by atomic absorption spectrophotometry.

X-ray diffraction patterns were taken on an INEL curved position sensitive CPS120 powder diffractometer in a horizontal Debye–Scherrer geometry using a rotating glass capillary 0.1 mm in diameter as sample holder. The angular range was 114° (2θ) and the radiation was Cu Kα₁ (λ = 1.540598 Å), obtained with a Ge (1 1 1) monochromator. The samples were sieved to 65 μm and in order to minimize the preferential orientation and absorption they were mixed with glass powder before filling the capillary. Rietveld refinements were performed using the Fullprof program [18].

Samples for transmission electron microscopy (TEM) were prepared by crushing the powder in hexane and dispersing the solution on a holey carbon film. Electron diffraction (ED) and high-resolution electron microscopy (HREM) were performed using a Jeol 4000EX microscope operating at 400 kV. Computer simulated images for different defocus and different thicknesses were obtained using the Crystalkit and MacTempas program.

Magnetic susceptibility measurements were performed in a Quantum Design SQUID magnetometer down to 4 K on double sealed samples in zero field cooled and field cooled conditions (H = 30 G).

3. Results and discussion

The observed and calculated X-ray diffraction patterns for a sodium intercalated sample containing the stages 1 and 2 phases are shown in Fig. 1. Magnetic susceptibility measurements for this sample (Fig. 2) show bulk superconductivity with a critical temperature (onset) of 24 K. Results of chemical analyses gave a stoichiometry of
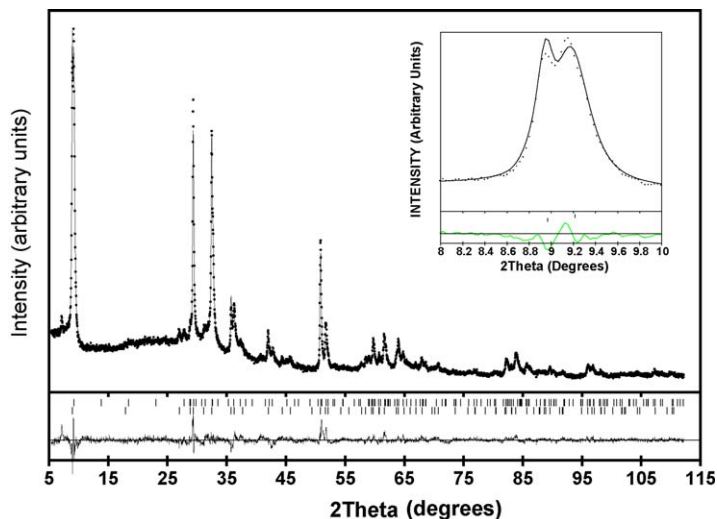
Fig. 1. Observed and calculated X-ray diffraction patterns for a sodium intercalated sample of HfNCl containing the stage 1 and stage 2 phases in refined fractions of 31.5% and 68.5%, respectively. The inset shows a zoom of the 0 0 3 reflection (0 0 6 reflection for the stage 2 phase).

0.32 sodium atoms per formula. The proportions obtained in the Rietveld refinement for stage 1 and stage 2 phases were 31.5% and 68.5%, respectively. In Table 1 we show the crystallographic and refinement data for both compounds. For the stage 1 phase we used the crystal data of $Na_{0.29}HfNCl$ reported by Shamoto et al. as starting parameters in the refinement [8]. The refined parameters for the stage 1 phase were slightly smaller than those reported by Shamoto et al. ($c = 29.6785(17)$ Å (this work) versus $29.722(3)$ Å [8]). For the stage 2 phase an ordered structure was refined, doubling the c parameter ($a = 3.58131(6)$ Å, $c = 57.752(6)$ Å), two crystallographically independent [HfNCl] units and the sodium atoms occupying octahedral positions in alternating van der Waals gaps [17]. The stoichiometries were fixed during the refinement to $Na_{0.25}HfNCl$ and $Na_{0.125}HfNCl$ for the stages 1 and 2 respectively. The sodium content obtained by chemical analysis, between 0.25 and 0.5 atoms per formula, agrees with the expected values considering the occupancy of the octahedral sites (0 0 0) in the van der Waals gaps. Full occupancy for these sites gives 0.5 sodium atoms per formula that is the maximum sodium content expected for the stage 1 phase, whereas full occupancy of the same sites in alternating van der Waals gaps would give a sodium
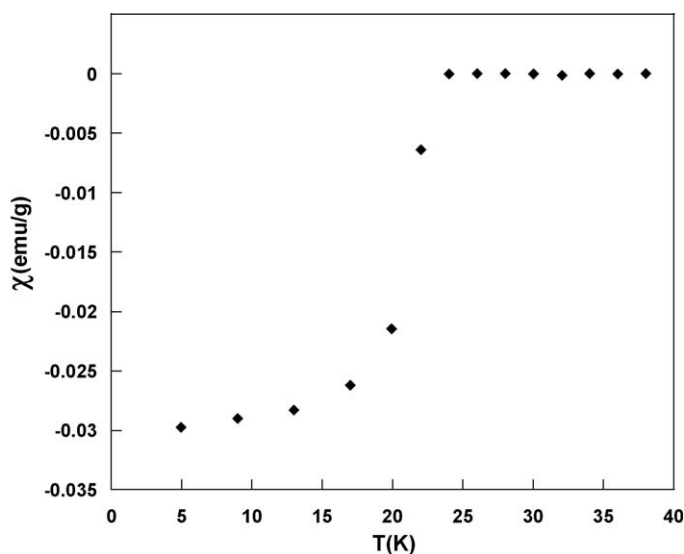

Fig. 2. Magnetic susceptibility for $Na_{0.32}HfNCl$, containing the stage 1 and stage 2 phases.

Table 1
Crystallographic and refinement data for stages 1 and 2 of sodium intercalated HfNCl

Stage 1
  Crystal data
    Space group $R\bar{3}m$ (N° 166), $Na_{0.25}HfNCl$, $Z = 6$
    a (Å) 3.58791(8)
    c (Å) 29.6785(17)

Atom coordinates

Atom	Site	x/a	y/b	z/c	Occupancy	B (Å^2)
Hf	6c	0	0	0.21025(19)	1	0.60
Cl	6c	0	0	0.3892(7)	1	0.60
N	6c	0	0	0.137(2)	1	0.59
Na	3a	0	0	0	0.25	0.59

Stage 2
  Crystal data
    Space group $R\bar{3}m$ (N° 166), $Na_{0.125}HfNCl$, $Z = 12$
    a (Å) 3.58131(6)
    c (Å) 57.752(6)

Atom coordinates

Atom	Site	x/a	y/b	z/c	Occupancy	B (Å^2)
Hf1	6c	0	0	0.39677(2)	1	0.56
Hf2	6c	0	0	0.10499(2)	1	0.56
Cl1	6c	0	0	0.19537(1)	1	0.60
Cl2	6c	0	0	0.30237(1)	1	0.60
N1	6c	0	0	0.06909(2)	1	0.59
N2	6c	0	0	0.43592(2)	1	0.59
Na	3a	0	0	0	0.25	0.59

Refinement data
  λ(Å) 1.54060
  2θ range, step $0.28 \leq 2\theta \leq 114.7$, 0.029
  N_p 3947
  N_{refl}[a] Stage 1: 84; stage 2: 159
  P_p, P_i, P_g[b] 19, 9, 0
  R_{Bragg}, R_F Stage 1: 9.27, 6.2; stage 2: 4.13, 2.9
  $R_p, R_{wp}, R_{exp}, \chi^2$[c] 19.6, 17.8, 11.2, 2.5

[a] N_p, N_{refl}, N_{irefl} refer to the number of experimental points, total reflections and independent reflections, respectively.

[b] P_p, P_i, P_g, refer to the number of profile, intensity-dependent and global refined parameters, respectively. The profile fitting of the data was performed with a pseudo-Voigt function, including asymmetry and preferred orientation corrections. Preferred orientation and asymmetry were corrected respectively by the March–Dollase and the Berar–Bardinozzi expressions.

[c] Conventional Rietveld R-factors (R_p, R_{wp}, R_{exp}) are calculated by using background corrected counts (see Ref. [18] for definitions).

content of 0.25 that is the maximum expected for the stage 2. For the refinement we have considered 50% of occupancy of the sodium sites in both phases.

For the stage 2 phase soft constraints were applied to the following bond distances: Hf(1)–Cl(1), Hf(1)–N(1), N(1)–Cl(2), Hf(2)–Cl(1), Hf(2)–N(2) and N(2)–Cl(1). However, the two [HfNCl] units were left to refine freely and independently. Fig. 3 shows a projection of the structures along [1 0 0] together with the structure of the host, β-HfNCl [1]. The coordination polyhedra around the Hf atoms in the double layers [Cl–Hf–N–N–Hf–Cl] and the relevant bond distances for the three structures are shown in Fig. 4. Hafnium atoms are heptacoordinated by three chlorine and three nitrogen atoms in one [HfNCl] layer and by one additional nitrogen atom from the second [HfNCl] layer. The Hf–N distances for stage 1 and stage 2 compounds as well as for the pristine are generally shorter inside one [HfNCl] layer than along the c direction. One of the most significant differences between the host and the intercalated phases is shown by the Hf–Cl distances that are longer when sodium is intercalated, as a consequence of the bonding between the chlorine and the sodium atoms. The heavy atoms in the pristine show the SmSI polytype, with the same packing as
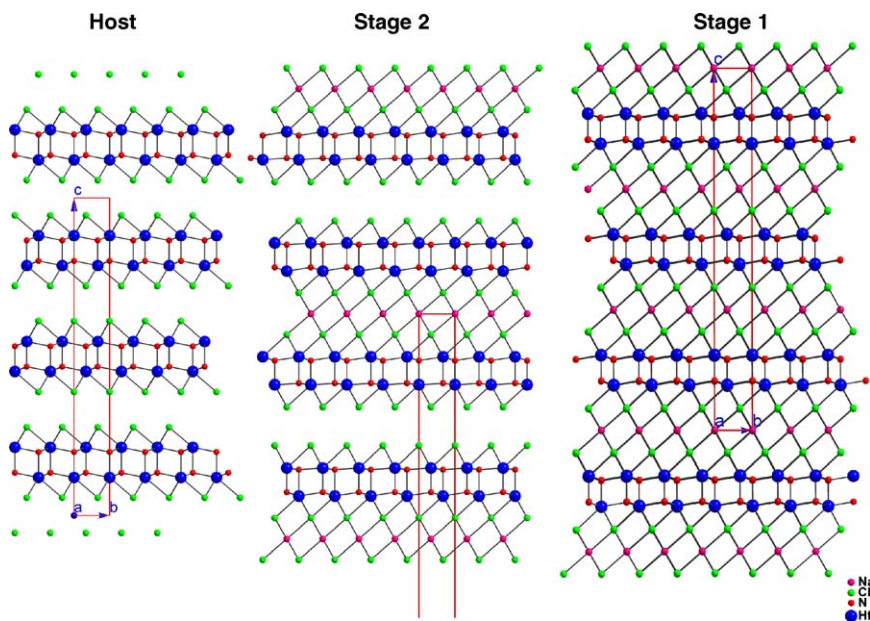
Fig. 3. Crystal structures projected along [100] of β-HfNCl, stage 2 of sodium intercalated HfNCl, and stage 1 of sodium intercalated HfNCl.

in ZrCl, where the double layers [X–M–M–X] have a stacking sequence ...ABC... In the intercalated phases they adopt the packing of the ZrBr structure with the double layers packed with relative stacking sequence ...ABC... [19,20,21]. The SmSI polytype is not energetically favoured in zirconium and hafnium nitride halides when significant intercalation takes place, which induces a structural phase transition to the YOF polytype. This is also the case for
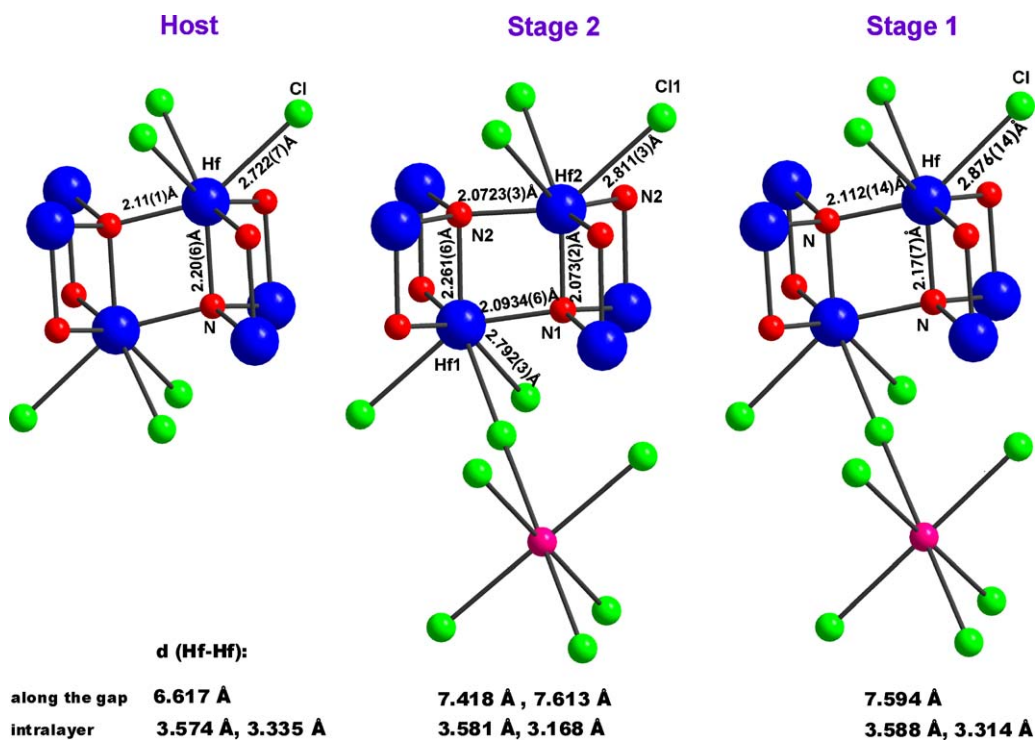

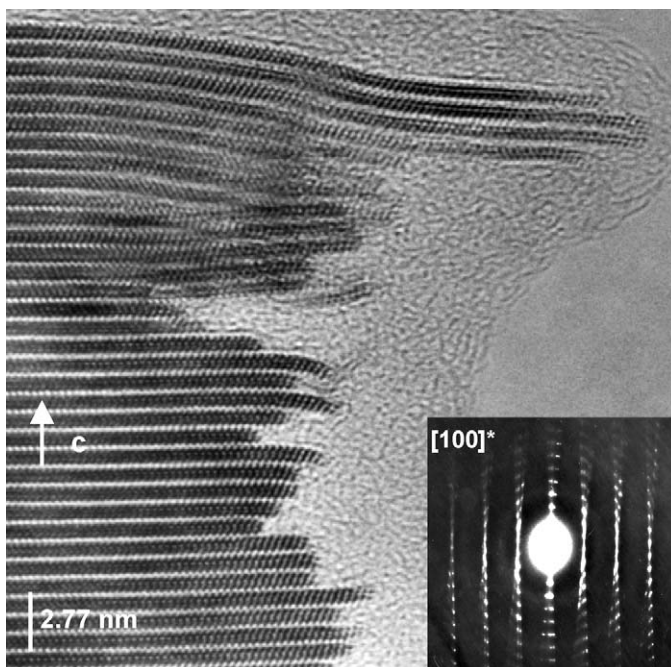Fig. 4. Co-ordination polyhedra of hafnium atoms in β-HfNCl and in the stage 2 and stage 1 phases of Na$_x$HfNCl.

Fig. 5. High-resolution electron microscopy image along [1 0 0] for the compound β-HfNCl showing bending of the HfNCl double layers at the crystal edge. Inset: corresponding electron diffraction pattern.
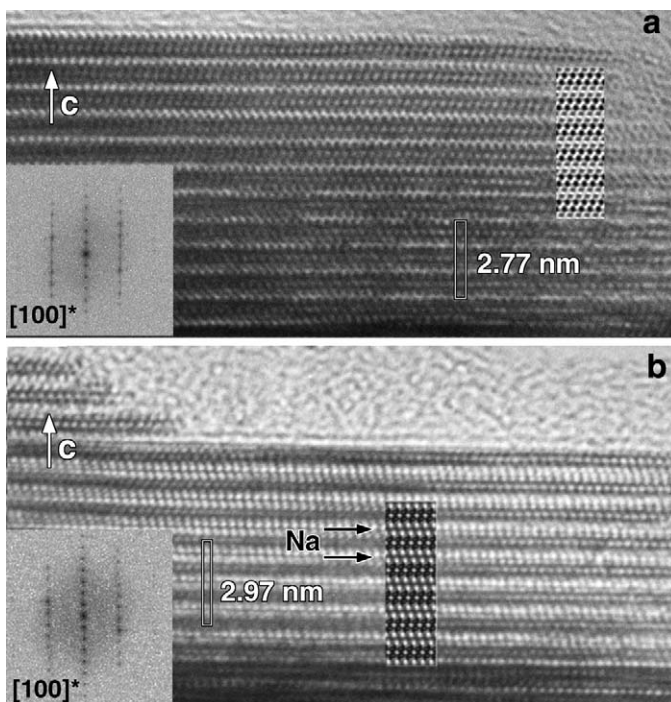

Fig. 6. High-resolution electron microscopy images along [1 0 0] for (a) β-HfNCl; (b) the stage 1 phase of Na_xHfNCl. The calculated images for focus −40 nm and a thickness of 4 nm model in β-HfNCl and for −45 nm and a thickness of 12 nm model in Na_xHfNCl are shown in the respective experimental images. Insets show the corresponding Fourier transforms.

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isostructural rare earth oxyhalides [22], and a general explanation for such behaviour is that in the SmSI polytype the second nearest neighbours for the intercalated atoms in the octahedral sites of the van der Waals gaps are Hf, Zr, Y and lanthanide atoms. In the YOF polytype the stacking of the double layers along the c axis is different and the second nearest neighbours for the intercalated atoms are nitrogen or oxygen atoms instead of metal atoms. The average interlayer spacing for the two phases are 9.8928(17) Å (Stage 1) and 9.625(6) Å (Stage 2). The Hf–Hf distances along the van der Waals gap (i.e. between Hf atoms in different double layers [Cl–Hf–N–N–Hf–Cl]) are consistent with the different occupancies of sodium atoms in each phase. In the host compound this distance is 6.617 Å, in the first stage phase it is 7.594 Å, and in the second stage phase two alternating distances result, along an occupied van der Waals gap, 7.613 Å and along an empty gap, 7.418 Å.

Fig. 5 shows a high-resolution electron microscopy image of the host compound along the [1 0 0]* zone axis. The [Cl–Hf–N–N–Hf–Cl] double layers show an ordered stacking along the *c*-axis in the inner part of the crystals and stacking faults at the edges, with remarkable bending of the layers. In the electron diffraction pattern (inset of Fig. 5) this bending result in arc shaped reflections away from the origin. In Fig. 6 we show a HREM image for the host compound as well as for a sodium intercalated sample of HfNCl. For the image simulation in the sodium intercalated sample we used the structure model of the stage 1 phase that shows a good correspondence with the experimental image. The intense bright dots in the intercalated compound correspond to the Cl configuration and the less intense dots are assigned to the Hf atoms. In the simulated image for the host structure the intense dark dots correspond to the Cl configuration and the less dark ones are Hf. Precise measurements for the c axis were performed on the Fourier transforms shown as inset in Fig. 6 and they agreed with the parameters for the host and the stage 1 phase respectively. The image of the intercalated sample in Fig. 6 represents the first HREM observation of a superconducting intercalate of HfNCl. However, the possible existence in these samples of Hérold–Dumas domains proposed for instance in staged graphite intercalation compounds [14], as well as the elucidation of the mechanisms allowing the coexistence of the host, the stage 1 and stage 2 phases in the same sample–as extended defects or as separated crystals-deserve certainly further attention and continued HREM work.

Acknowledgements

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