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Crystal structures of superconducting sodium intercalates of hafnium nitride chloride

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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.

Keywords: A. Nitrides; A. Superconductors; B. Intercalation reactions; D. Crystal structure

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 Kα_1 ($\lambda = 1.540598$ 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