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**Intercalation and superconductivity in ternary layer structured metal nitride halides ( $MNX$ :  $M =$   
**Ti, Zr, Hf;  $X =$  Cl, Br, I )****

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There are two types of layer structured polymorphs in the title ternary compounds: the  $\alpha$ -form with the FeOCl structure and the  $\beta$ -form with the SmSI structure. These crystals are semiconductors with band gaps of about 2-4 eV. The  $\beta$ -form has a honeycomb-like metal nitride ( $MN$ ) layered network, and is changed into superconductors by electron doping. The superconducting transition temperatures ( $T_c$ s) are 13-15 K, and about 25 K for  $\beta$ -ZrNCl and  $\beta$ -HfNCl, respectively. The electron doping can be done by intercalation of alkali metals or deintercalation of chlorine atoms from the interlayer space between the nitride layers. The alkali metal intercalated compounds can be co-intercalated with various solvent molecules; the  $T_c$  increases upon swelling with solvent molecules, the anisotropy of the superconductivity being significantly increased. TiNCl adopts only the  $\alpha$ -form structure. In contrast to the honeycomb network of  $\beta$ -ZrNCl and HfNCl, TiNCl has orthogonal nitride layers. TiNCl can also be changed into superconductors with  $T_c$ s of 8.6 and  $\sim$ 16.3 K upon electron-doping by means of intercalation of pyridine, and alkali metals, respectively. Superconductivity of TiNCl intercalated with a series of amines will also be introduced.