New developments in N-containing phases: nitrides, cyanides, and more

Peter Höhn[#], Matej Bobnar, Natalia Glorizova, Franziska Jach, Primož Koželj, Alim Ormeci, Alexander Ovchinnikov, Manisha Pathak, Yurii Prots, and Frank R. Wagner

The focus on nitride research remains on exploratory work on nitridometalates, multianionic compounds such as nitride-gallides, and similar phases under conditions reaching from strongly oxidizing to highly reducing. Our investigations on these chemically and structurally interesting and experimentally challenging systems containing very air- and moisture-sensitive phases are highlighted by host phases able to contain both anionic or cationic species, highly anisotropic magnetic properties in nitridometalates, as well as unprecedented Ge-Ge-bonds in nitridogermanates(III).

The versatility of the Ba₃[FeN₃]-type structure: nitridometalates vs. highly reduced cyanometalates

The crystal structure of $Ba_3[FeN_3]$ (Fig. 1a) is characterized by trigonal-planar anions and large empty channels along [001] built up by octahedral voids and bordered by Ba and N, providing a convenient host for a plethora of charged species.

Both the nitridometalate-fluorides $Sr_3[CrN_3]F_x$ [1] and $Ba_3[CrN_3]F_x$ [1] as well as the highly reduced cyanides $LiSr_3[Fe(CN)_3]$ [2] and $Ba_{3.5}[Fe(CN)_3]$ [2] were prepared by solid state routes from the elements and binary nitrides.

In the nitridometalate-fluorides (Fig. 1b), a progressing occupation of the octahedral voids with fluoride species (Fig. 1c) is accompanied by a concomitant increase in the c/a ratio and presumably correlated with a gradual oxidation from $Cr^{3+} \rightarrow Cr^{4+}$. In case of $Sr_3[CrN_3]F_x$, for x > 0.7 (Fig. 1d), a nine-fold rhombohedral superstructure evolves.

In contrast, in the electron-precise highly reduced cyanometallates, upon substitution of $Co^- d^{10}$ in

 AE_3 [Co(CN)₃] by Fe²⁻ d^{10} , the octahedral voids are either fully occupied by Li⁺ (Fig. 1e) or half occupied by Ba²⁺ in a complex superstructure (Fig. 1f).

Magnetic anisotropy in nitridometalates

The formation of local magnetic moments in solids has implications that range from nanoscale data storage devices to massive hard magnets. Those materials usually require the presence of heavy transition-metal or rare-earth elements in order to provide a sufficiently large magnetic anisotropy. The origin of the desired magnetic stability lies in an orbital contribution to the magnetic moment. Although in 3*d* transition-metal compounds this contribution is normally almost fully suppressed by the crystal electric field, orbital moments, which give rise to large magnetic anisotropy, are frequently observed in low-valent nitridometalates.

Large single crystals of both LiSr₂[CoN₂] [3] (Fig. 2a) and Li₂Sr[MnN]₂ [4] (Fig. 2b) were successfully grown in Li-rich flux employing the HTCAF (High Temperature Centrifugation Aided Filtration) method.



Fig. 1: Variations on a theme: a) $Ba_3[FeN_3]$: empty channels; b) $Ba_3[CrN_3]F$: channels successively filled with anions; c) c/a ratio in $AE_3[CrN_3]F_x$ as a function of x; d) $Sr_3[CrN_3]F$: channels successively filled with anions, nine-fold superstructure; e) $LiSr_3[Fe(CN)_3]$: channels completely filled with cations; f) $Ba_{3.5}[Fe(CN)_3]$: channels half-filled with cations, three-fold structurally frustrated superstructure.



Fig. 2: Crystal structures of a) $LiSr_2[CoN_2]$ and b) $Li_2Sr[MnN]_2$; Magnetic susceptibilities of c) $LiSr_2[CoN_2]$ and d) $Li_2Sr[MnN]_2$ with field applied perpendicular and parallel to the crystallographic c-axis.

Albeit different, both crystal structures feature arrays of alternating layers of (almost) linear -N-M-N-M/Li-N- chains as central structural motifs.

In $LiSr_2[CoN_2]$ (Fig. 2c), ferromagnetic ordering emerges below $T_C = 43$ K and comparatively large coercivity fields of $\mu_0 H = 0.3$ T as well as pronounced anisotropy are observed upon cooling. Co manifests orbital contributions to the magnetic moment that are unquenched due to 2nd order spin-orbit coupling. In Li₂Sr[MnN]₂ (Fig. 2d), both the electronic and magnetic properties are most remarkable, in particular the linear increase of the magnetic susceptibility with temperature which is reminiscent of underdoped cuprate and Fe-based superconductors. Clear indications for antiferromagnetic ordering at $T_N = 290$ K were obtained. Metallic transport behavior is experimentally observed in accordance with electronic band structure calculations.

Nitridometalates vs. multianionic nitrides

Multinary systems (Li-)*AE-M*-N (AE = Ca, Sr, Ba; M = Ga, Ge) provide a playground for a plethora of phases with highly differing structural features and physical properties. Depending on the nitrogen content of a sample, the oxidation states of the metalloids can be so precisely set that germanide nitrides Sr₃N_{0.67}Pb and gallide nitrides such as LiSr₃[Ga₂]N are accessible in the low-nitrogen range, whereas in the higher-nitrogen range unusual oxidation states can also be



Fig. 3: ELI distribution in the hexagonal unit cell of $Sr_6[Ge_2N_6]$ (isosurface value 1.38). The 2D plot of ELI in the (a,c) plane highlights the structuring of the penultimate shell (n = 4) of the Sr atoms.

stabilized, such as Ge^{III} in the nitridogermanate $Sr_6[Ge_2N_6]$ [5] (Fig. 3).

Attempts to synthesize nitridoaurates from binary nitrides and gold by HTCAF in lithium melts did not succeed, but instead led to large single crystals of $\text{Li}A_E\text{Au}$ (A_E = Ca, Sr, Ba, Yb, Eu) with TiNiSi type structure; however, this developing story will be a topic of our future research.

External Cooperation Partners

Michael Ruck, Lukas M. Eng (TU Dresden); Anton Jesche (Universität Augsburg); Rainer Niewa (Universität Stuttgart); Mehmet Somer (Koç University, Istanbul).

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[#] Peter.Hoehn@cpfs.mpg.de