[N_2^{2-}] – Dumb-Bells Trapped within a Cage of Alkaline-Earth Metals

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In the course of our work on binary alkaline-earth metal diazenides, Sr_4N_3 – a hitherto missing member in the nitrogen pressure reaction series $Sr_2N \rightarrow Sr_4N_3 \rightarrow SrN \rightarrow SrN_2$ (see Fig.1) [1, 2] – was discovered by chemical analysis with a modified carrier gas hot extraction method [3] (see ***"Chemical Analysis – Quantitative Speciation of Nitrogen"***). By using Sr_2N as starting material and increasing N_2-pressures at a temperature of 920 K a stepwise oxidation of strontium to Sr^{2+} takes place together with a reduction of molecular nitrogen to N_2^{2-}. The compounds were obtained as single phase products. The crystal structures of the air- and moisture-sensitive microcrystalline powders were determined by a combination of X-ray and neutron diffraction experiments at ambient conditions. The evident structural relation makes it reasonable to suppose the reaction paths of the formation of nitride diazenides via intercalation steps. $Sr_4N_3 < Sr_8[N]_4[N_2]$ (9 bar) represents the first intercalation stage of the Sr_2N host structure followed by the second intercalation step $SrN < Sr_8[N]_4[N_2]_2$ (400 bar). At the highest reaction pressure SrN_2 (5500 bar), a pure diazenide, is formed. All reactions under consideration are reversible.

The formation of Sr_4N_3 can be described in principle by the occupation of two different octahedral holes within the layers. Evidently, the spatial separation of the diazenide layers makes an alternative occupation of the octahedral holes possible although within every layer the same kind of octahedral holes are always occupied. In fact, the diffraction patterns indicate a ***C***-centered cell, thus leading to a half-occupation of all the octahedral holes by the [N_2^{2-}] species. As shown in Fig. 2 every second $Sr_{6/3}N$-octahedral layer remains empty. In the crystal structure of SrN half of the octahedral holes of every empty layer is now occupied by [N_2^{2-}]-units. Finally in SrN_2 all octahedral holes including the holes formerly occupied by the [N^{3-}]-units are filled with [N_2^{2-}]-dumb-bells [1,4].

The [N_2^{2-}]-dumb-bells are trapped within octahedral cages of strontium. Therefore, an interesting question is whether they behave similar to the "guest" atoms in the clathrates (see ***"Progress in Clathrate Research"***) as so-called "rattlers", i.e., as entities which perform large thermal motions somewhat independently of the framework or the "host" atoms. This kind of local oscillation ("rattling") may be modeled by an Einstein oscillator.

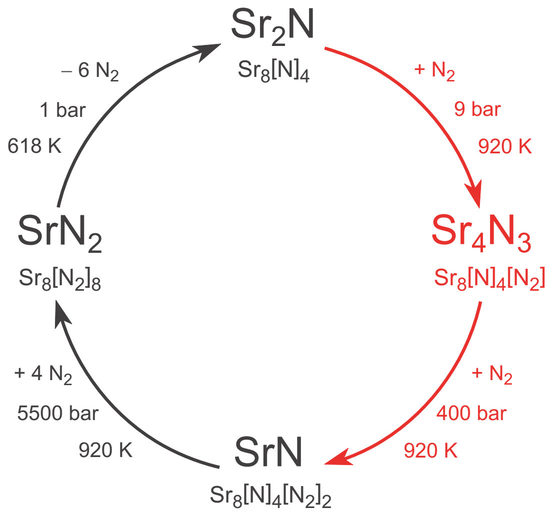

Fig. 1: Reaction conditions for the high-pressure series in the system Sr-N. Red: Hithero missing member [2].

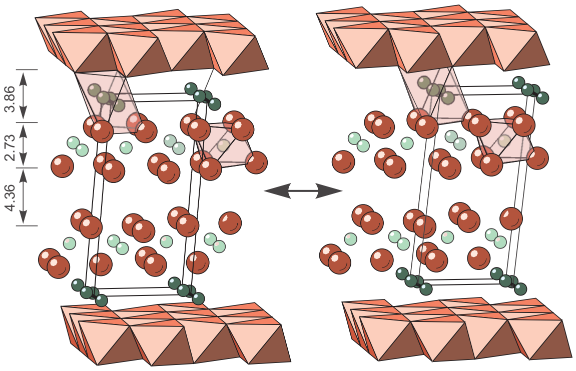

Fig. 2: Crystal structure of Sr_4N_3 = $Sr_8[N]_4[N_2]$. The top and bottom boundaries of the figures are represented by layers of $Sr_{6/3}$ octahedra centered by [N] (polyhedral representation). Ball- and stick representation is used between the polyhedral layers. Sr: red; [N]: light green, [N_2]: dark green. Transparent octahedra allow a better visual orientation. On the assumption of ordered [N_2] occupation, the two limiting primitive structures are

The interest in compounds containing “rattlers” stems from their potential for thermoelectric applications: The Einstein modes may resonantly scatter acoustic mode heat-carrying phonons leading to a low and “glass-like” thermal conductivity – a prerequisite for a good thermoelectric material.

In order to test whether “rattling” is indeed relevant for SrN and/or Sr_4N_3 we have measured the temperature dependence of the specific heat. Since the samples are air and moisture sensitive, pellets were pressed and mounted on the sample holder under argon atmosphere. The measurements were performed under He gas. The data taken upon cooling and warming were identical indicating that the sample quality was unchanged during the measurement. The specific heat data of both SrN and Sr_4N_3 are displayed in Fig. 3. Below 10 K the data may be well approximated by $C_p/T = \gamma + \beta T^2$, where the Sommerfeld coefficient γ and the βT^2 term describe the low-temperature electronic and phononic contributions, respectively. The γ coefficients of approximately 1 (5) $mJ/gatK^2$ for SrN (Sr_4N_3) indicate that both materials are metals. The Debye temperatures estimated from the β coefficients (approximately 0.08 $mJ/gatK^4$ are 290 K for both compounds. Fitting the $C_p(T)$ data with a Debye contribution (for the framework atoms) and an Einstein contribution (for the “rattlers”) we obtain Einstein temperatures larger than the highest temperatures of our measurements. The slight re-increase of the $C_p(T)$ curves above room temperature, instead of a smooth saturation to the Dulong and Petit value (DP), is the visual indication for the presence of such Einstein modes above room temperature. Thus, to confirm the existence of these modes the measurements would have to be extended to much higher temperatures where, however, the material decomposes (DTA measurements). Alternatively, spectroscopic measurements (e.g., Raman or inelastic neutron scattering) can be used to probe these excitations.

All attempts to record Raman spectra of Sr_4N_3, SrN and SrN_2 failed although different laser frequencies, low temperature and different sample preparation conditions were used. This may be due to reflection or absorption of the laser beam by these intensely dark-colored powders. After synthesizing about 25g of SrN and SrN_2 each, success was achieved by the first inelastic neutron scattering studies on using the time-of-flight spectrometers TOSCA and MARI (Rutherford Appleton Laboratory, UK). The intensity of the inelastic neutron scattering spectra does not depend on electronic properties such as dipole moment or polarizability and hence, there are no symmetry-based selection rules and all modes are allowed, thus leading to rather complex spectra. For SrN_2 (tetragonal) a normal coordinate analysis using both energy and intensity information as constraints was carried out. By this, the local environment of the diazenide ion is modeled by placing it at the center of an octahedron of strontium ions and defining stretches between the Sr- and the N- and between adjacent Sr- species. The results are shown in Fig. 4

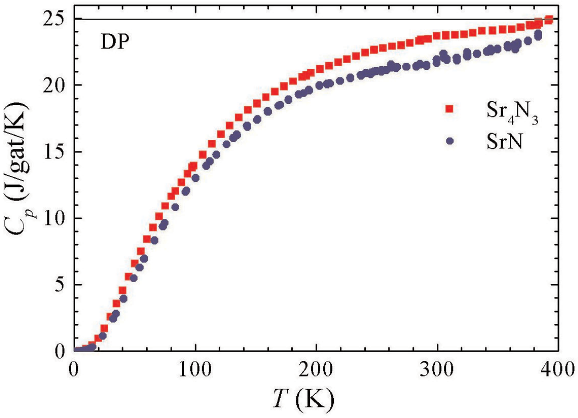

Fig. 3: Specific heat of Sr_4N_3 and SrN as a function of temperature.The Dulong and Petit value (DP) is given by the black line.

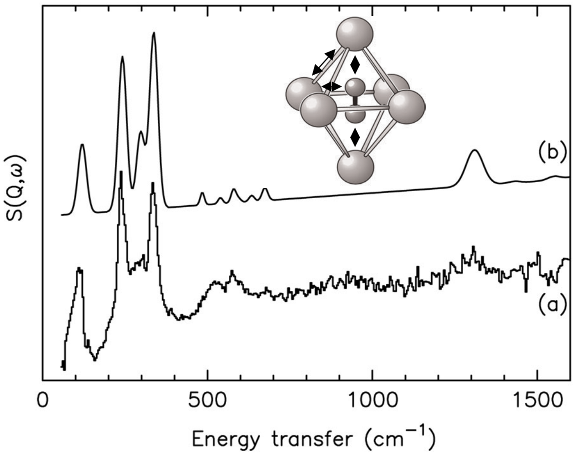

Fig. 4: a) Observed and b) calculated TOSCA inelastic neutron scattering (INS) spectra of SrN_2 [5]. The local environment of the diazenide ion in the center of an octahedron of strontium ions and the selected stretching modes used for normal coordinate analysis are inserted.

and it can be seen that the agreement is reasonable. In the case of SrN, the low symmetry of the crystal structure (monoclinic, $\boldsymbol{Z} = 4$) is reflected in the complexity of the spectra. Therefore, a large number of features below 600 cm^{-1} due to the translational modes of the ions and the librations of the diazenide ion becomes obvious. The rattling mode for the $[N_2^{2-}]$ could be assigend to features at 303 cm^{-1} (436 K) for SrN and at 337 cm^{-1} (485 K) for SrN_2. The N=N stretch of the diazenide ion was assigned to a feature at 1380 cm^{-1} for SrN and at 1307 cm^{-1} for SrN_2. These values are in good agreement with that of singlet-diazenide-units in organometallic compounds ($\nu = 1350$ cm^{-1}).

Further investigations to vary the physical properties of the strontium diazenides were carried out in the system Sr-Sm-N (possible substitution of strontium against samarium) [6]. After arc-melting the two metals (no reaction of Sr_2N and SmN was observed) the syntheses succeed in analogy to the binary strontium nitrogen system. Up to a maximal content of 5 at% Sm a homogenous distribution of Sm and Sr is observed (EDX, element mapping). Neutron diffraction experiments revealed the formation of ternary substituted phases $(Sr_{1-2\boldsymbol{x}}Sm_{\boldsymbol{x}})_2N$ and $(Sr_{1-2\boldsymbol{x}}Sm_{\boldsymbol{x}})_4N_3$, $0 \leq \boldsymbol{x} \leq 0.05$ which are isotypes of Sr_2N and Sr_4N_3 with a partially vacant cation framework. These observations were confirmed by chemical analyses. The chemical peculiarity of the ternary substitutional phases is visible in the higher reactivity with molecular nitrogen. Thus, the samarium substituted subnitride (Sr_2N structure type) reacts already in a stream of nitrogen (1 bar) to the first intercalation step (Sr_4N_3 structure type). Assuming that Sr^{2+} is partially substituted by Sm^{3+}, vacancies at the cation sites occur (confirmed by structure refinements), which could be responsible for the higher reactivity.

Additional studies within the system Ba-N show clearly that starting from Ba_2N elevated N_2-reaction pressures lead to the insertion of $[N_2^{2-}]$ dumbbells in the host structure in the same way. The pressure regions for obtaining pure phases are smaller. The pure diazenide BaN_2 [7] can already be prepared at 400 bar N_2 whereas in the pressure range 4 bar – 12 bar reveals the existence of Ba_4N_3 and BaN is observed, a result which was confirmed by neutron diffraction experiments. The crystal structures of Ba_4N_3, BaN and BaN_2 [7] differ from those of the analogous strontium nitrogen phases (differences in the orientation of the $[N_2]$ dumb-bells).

The extension of this work to single crystal investigations is in progress. These complementary studies should finally confirm the topochemical host-guest relations for intercalation and deintercalation in the course of formation of the alkaline-earth nitride-diazenides.

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