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New quasi-2D nickel-gallium mixed chalcogenides based on the Cu_3Au-type extended fragments

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Three new mixed nickel-gallium chalcogenides, $Ni_{6.10}GaS_2$ (*I4/mmm*, $a = 3.5310(5)$ Å, $c = 17.968(4)$ Å, Z = 2, $R_1 = 0.014$), $Ni_{5.63}GaSe_2$ (*I4/mmm*, $a = 3.5995(3)$ Å, $c = 18.517(3)$ Å, Z = 2, $R_1 = 0.018$), and $Ni_{8.54}Ga_2Se_2$ (*I4/mmm*, $a = 3.5810(5)$ Å, $c = 25.506(5)$ Å, Z = 2, $R_1 = 0.028$), have been synthesized by a high-temperature ampoule route and characterized from single-crystal diffraction data, with their compositions supported by the EDS data. They belong to the relatively rare $Ni_{7-x}MQ_2/Ni_{10-x}M_2Q_2$ type of structures (M=Ge, Sn, Sb, In), and are built from gallium-centered nickel cuboctahedra of the Cu_3Au type, alternating along the *c* axis with either nickel-sulfur fragments of the Li_2O and Cu_2Sb/NaCl types, or with nickel-selenium fragments of the Cu_2Sb/NaCl type. DFT calculations show close relationship of electronic structures of these ternary compounds to their parent intermetallic, Ni_3Ga. Metallic conductivity and paramagnetic properties are predicted for all three. The bonding pattern, investigated via the ELI-D topological analysis, shows the multi-centered nickel-gallium bonds in the Cu_3Au-type fragments. Magnetic measurements on $Ni_{5.63}GaSe_2$ show it to have an antiferromagnetic transition at 7 K and to obey the Curie-Weiss law above 160 K.

1. Introduction

Due to their incredible structural diversity and variety of physical properties, ordered intermetallic compounds have the potential to provide exciting objects of studies for several generations of chemists, both theoretically (due to often complicated crystal structures and highly unconventional bonding patterns) and practically (due to often unique and useful physical properties and convoluted structure-property relationship) minded. Yet, if we dilute a 3D intermetallic system with a typical non-metal (pnictogen or chalcogen), adding possible effects of reduced dimensionality into the mix, the situation becomes even less straightforward. This concept can be showcased pretty well using the so-called 'quasi-2D' mixed group 10 – group 13-15 chalcogenides and pnictides of the $T_{7-x}MQ_2$, $Ni_{10-x}M_2Q_2$ (for T=Ni, M=Si, Ge, Sn, Sb, In, and Q=S, Se, Te; for T=Pd, M=Sn, and Q=Te) [1–7], Pd_5TlAs [8–10], and Pd_8In_2Se [9,10] families. A scheme of formation of the nickel-based types of structures from their building blocks is given in Fig. 1. All these compounds crystallize in the tetragonal system and feature main-group metal-centered $[T_{12}M]$ cuboctahedral fragments of the Cu_3Au type as main structural units. These cuboctahedra form layers in the *ab* plane of a unit cell, alternating along the *c* axis with transition metal – chalcogen or transition metal – pnictogen layers of various types, namely: antifluorite-plus defective Cu_2Sb-type (nickel-based sulfides [2,5]), defective Cu_2Sb-type (nickel-based selenides and tellurides [1,3–5,7], and palladium-tin telluride [6]), or $PtHg_2$-type [8–10]. In the $T_{7-x}MQ_2$- and Pd_5TlAs-type structures these layers are only one cuboctahedron high, while in $Ni_{10-x}M_2Q_2$-and Pd_8In_2Se-types these polyhedra are double-stacked along the *c* axis. A single exception from this structure pattern so far has been $Pd_{17}In_4Se_4$ [10], another metal-rich palladium-indium selenide that is also based on the Cu_3Au-type fragments, however, selenium, rather than forming metal-chalcogen blocks, terminates heterometallic ones and thus facilitates the formation of the open-framework structure with 1D channels running through. Another common

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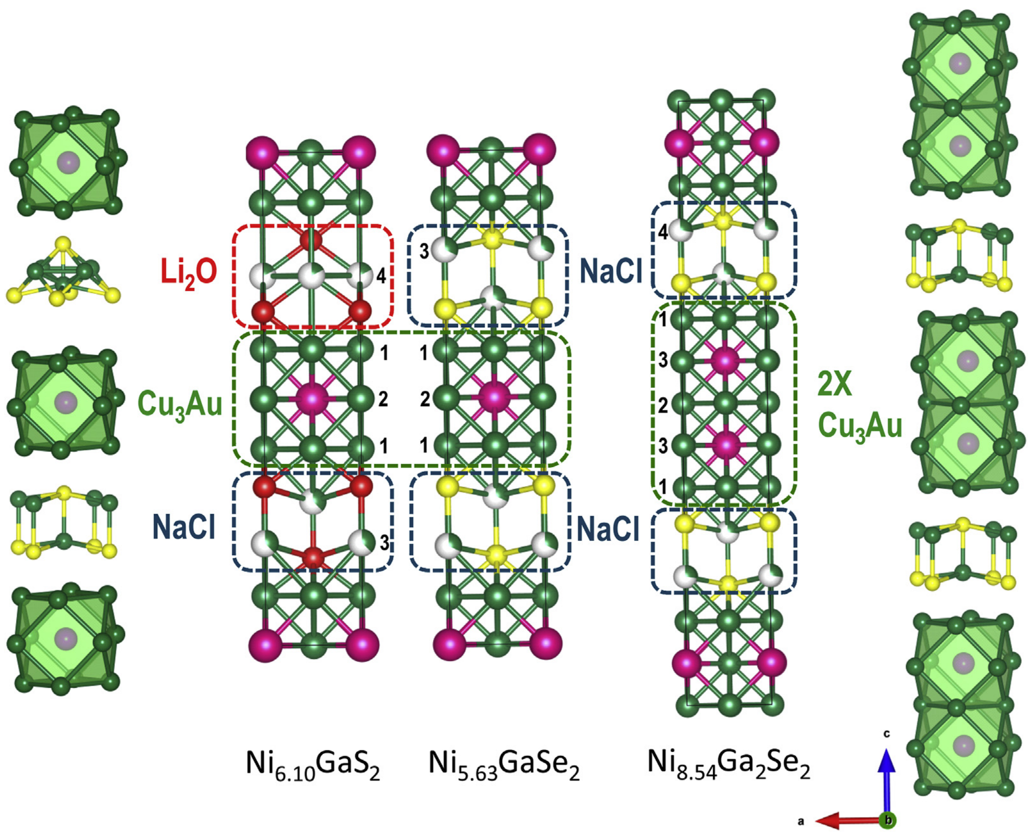

Fig. 1. Unit cells and structural fragments of $Ni_{6.10}GaS_2$, $Ni_{5.63}GaSe_2$, and $Ni_{8.54}Ga_2Se_2$. Green balls represent nickel, pink – gallium, red – sulfur, and yellow – selenium. Balls with green sectors represent partially occupied nickel positions. Numbers near nickel atoms denote their crystallographic positions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

feature of all the $T_{7-x}MQ_2$- and $Ni_{10-x}M_2Q_2$-type is that they were all proven to be non-stoichiometric with respect to nickel (where for all Ni-based phases $x \geq 1$), yet they have extremely narrow homogeneity range. Theoretical calculations predicted all compounds to exhibit 3D metallic conductivity and possible paramagnetic behavior, which was for selected compounds confirmed by the electric conductivity [1,3,4,7] and magnetic susceptibility [1,3] measurements. The lack of experimental characterization of physical properties is not surprising, since the majority of the compounds in question was reported to have been very difficult to obtain as phase-pure bulk samples, and some of the $Ni_{10-x}M_2Q_2$-type phases were proven metastable [5].

When comparing the behavior of nickel to platinum and palladium regarding the formation of the compounds featuring the cuboctahedral Cu_3Au-type fragments, it is clear that the former tends to adopt the $T_{7-x}MQ_2$- and $Ni_{10-x}M_2Q_2$-type structures, while the two latter show the preference towards Pd_5TlAs variations. Also, while palladium and platinum form many such compounds with group 13 metals [8–11], the abundance of nickel-rich compounds of the type in question with [$Ni_{12}M$] fragments of their parent intermetallics was found with group 14 and 15 metals, while the only group 13 compound of the $T_{7-x}MQ_2$-type is $Ni_{5.73}InSe_2$, that we have recently reported [7], and until then the most metal-rich ternary compounds in the nickel – group 13 metal – chalcogen systems were found to be $Ni_3In_2S_2$ [12] and $Ni_3Tl_2S_2$ [13], belonging to the different class of compounds – shandites with the 3D frameworks. As for the $Ni_{10-x}M_2Q_2$-type structures, so far none featured a group 13 metal.

As the result of our systematic search for nickel-rich mixed chalcogenides with group 13 metals, here we report the synthesis, crystal and electronic structure of three new compounds of this type, $Ni_{6.10}GaS_2$, $Ni_{5.63}GaSe_2$, and $Ni_{8.54}Ga_2Se_2$, along with magnetic properties of $Ni_{5.63}GaSe_2$.

2. Experimental

2.1. Synthetic and analytical procedures

Nickel (powder, 99.98%), gallium (shot, 99.999%), elemental sulfur (powder, 99.8%), and selenium (granules, 99.999%) were used for the synthesis. Prior to use, nickel powder was heated at 550 °C for 2 h in the flow of chromatographically pure hydrogen to remove potential traces of oxidation. The respective elements were mixed in the Ni:Ga:Q ratios of 6:1:2 and 9:2:2 (ca. 0.8 g in total per sample) and put into silica ampoules that were dried by heating under dynamic vacuum prior to use, sealed under vacuum (ca. 20 mTorr) and annealed for 7 days at 650 °C (±2 °C). After that the samples were left in the furnace as it cooled down to room temperature. Powder XRD data (Stoe STADI-P, $CuK_{\alpha1}$ radiation, $\lambda = 1.51053$ Å) have shown the similarities of the strong reflections in the patterns observed for 6:1:2 samples in both sulfur- and selenium-containing system to the patterns of Ni_6SnS_2 [2] and $Ni_{5.62}SnSe_2$ [3]. Powder patterns from both 9:2:2 samples were very similar, but featured large amounts of binary Ni_3Ga intermetallic, although none of the samples was phase pure, and all contained various quantities of binary intermetallics and chalcogenides. In order to improve the quality of the samples and eliminate impurities, all the products were thoroughly ground and pressed into pellets and annealed for another 7 days at the same temperature as before. After one more cycle of this procedure, only