

# Electronic structure and transport properties of novel Mo–Ru–Ge Nowotny chimney-ladder phases

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Incommensurate Nowotny chimney-ladder (NCL) phases are a unique group of intermetallic phases as their crystal structures exhibit lack of periodicity along one dimension [1]. Such aperiodicity opens an additional degree of freedom that might be utilized to optimize the physical properties. In addition, aperiodicity can potentially be used to obtain Slack's phonon-glass and electron-crystal behaviour, which is highly desirable in thermoelectric materials. However, despite the fact that numerous NCL phases have been identified, not so many, apart from higher manganese silicides (HMS) [1,2], have been studied from the perspective of thermoelectric properties.

In order to search for new representatives of the NCL phases in the Mo–Ru–Ge ternary system, we synthesized a sample with composition  $\text{Mo}_{11.9}\text{Ru}_{26.2}\text{Ge}_{61.9}$  by sintering powders of pure metals ( $\text{Mo} \geq 99.8$  wt.%,  $\text{Ru} \geq 99.9$  wt.%,  $\text{Ge} \geq 99.98$  wt.%) in vacuum-sealed quartz ampoules at 1000 °C for 4 days and at 800 °C for the next 5 days. X-ray powder diffraction data from a polycrystalline sample were obtained using a PROTO AXRD Benchtop diffractometer (Cu  $K\alpha_1$  radiation).

According to the phase analysis, the sample contained two ternary phases, the structures of which belonged to the chimney-ladder family. The compositions of both phases could be described as  $(\text{Mo}, \text{Ru})_8\text{Ge}_{13}$ , where (Mo, Ru) are statistical mixtures with close atomic ratios. A structure model of the chimney-ladder type was developed in the superspace group  $P: I4_1/amd(00ss): P4/nnc(q0q0)$  using the concept of modulated composite crystal structures in (3+1)-dimensional superspace [3]. The crystal structure can be represented as the interpenetration of two substructures, one formed by (Mo, Ru) (space group  $I4_1/amd$ ) and the other one by germanium atoms (space group  $P4/nnc$ ), implemented in the superspace group  $I4_1/amd(00\gamma)00ss$ . Using the WinCSD program package, commensurate approximants of the two phases were refined in space group  $P-4c2$  (Pearson symbol  $tP84$ ) with the following cell-parameters:  $a = 5.8570(8)$ ,  $c = 37.889(6)$  Å for the Mo-rich phase and  $a = 5.812(2)$ ,  $c = 37.34(2)$  Å for the Mo-poor phase.

We also present a theoretical study of the new ternary NCL phase of composition  $\text{Mo}_{2.5}\text{Ru}_{5.5}\text{Ge}_{13}$ . Ab-initio calculations of the electronic band structure, with spin-orbit interactions included, were performed using the all-electron full-potential linearized augmented plane wave (FP-LAPW) method, as implemented in the WIEN2k package. Transport properties were obtained using the constant relaxation time approximation within the BoltzTraP code. Our calculations showed that  $\text{Mo}_{2.5}\text{Ru}_{5.5}\text{Ge}_{13}$  has a relatively narrow bandgap, thus if the compound is properly doped it may possess semiconducting properties. Its multi-valley band structure as well as the Seebeck coefficient are heavily influenced by the location of the atoms in the Ge 'ladders', as indicated by calculations performed for the relaxed crystal structure.

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[3] Akselrud, L., Cardoso Gil, R., Wagner-Reetz, M. & Grin, Yu. (2015). *Acta Crystallogr. B* **71**, 707-712.

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