# Representatives of the Nowotny Chimney-Ladder phasesin the Mo–Ge system

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In the binary system Mo‒Ge, the existence of the compound Mo13Ge23 is known (space group *P*-4*n*2, Pearson symbol *tP*144, *a* = 5.987, *c* = 63.54 Å) [1]. The structure of this compound belongs to the Nowotny chimney-ladder phases, which were first described by Hans Nowotny. Nowotny chimney-ladder phases represent a class of composite compounds consisting of two substructures: a transition-metal element (*T*) of groups IVB-VIIIB and a *p*-block element (*M*) of main groups IIIA-VA. In these compounds, the transition-metal atoms form a substructure of the β-Sn type as the base of a “chimney”, around which atoms of the main group element twist to form helical chains as a “ladder”. Both substructures, with their respective lattice parameters *cT* and *cM*, are closely intertwined, creating the conditions for a homologous series of intergrowth compounds described in the tetragonal system with *a*-parameters in the range of 5.5 to 6.9 Å [2]. The *c*-parameter can take different values, reaching as much as 319 Å. This is because in a composite crystal, each substructure undergoes modulation (systematic displacement of atoms from their ideal positions in subsequent cells) as a result of the interactions [3]. In the Nowotny chimney-ladder phases, a one-dimensional modulation along the *c*-axis occurs. By combining structural fragments of the substructures in special ratios, commensurate approximants can be obtained.

The samples were synthesized by sintering powders of pure metals (Mo ≥ 99.8 wt.%, Ge ≥ 99.98 wt.%) in vacuum-sealed quartz ampoules at 1000 °C for 4 days and at 800 °C for the next 5 days, after which the ampoules were quenched in cold water. X-ray powder diffraction data from a polycrystalline sample was obtained using a PROTO AXRD Banchtop diffractometer (Cu *K*α1 radiation).

Two compounds were observed: Mo9Ge16 (space group *I*4122, Pearson symbol *tI*100, *a* = 5.99324(3), *c* = 44.0005(3) Å and Mo22Ge39, (*P*-4*c*2, *tP*244, *a* = 5.99119(4), *c* = 107.509(2) Å). The structures of these compounds also belong to the Nowotny chimney-ladder phases. The structure of Mo9Ge16 was refined as ordered and the unit cell consists of 9 pseudo-cells of the transition metal substructure (Mo) and 16 pseudo-cells of the main group element (Ge). The atomic coordinates and isotropic displacement parameters of the Mo9Ge16 compound are given in the table below. The structure of the Mo22Ge39 compound is incommensurately modulated and the approximant (average structure) consists of 22 pseudo-cells of the transition metal substructure (Mo) and 39 pseudo-cells of the main group element (Ge), the combination of which gives a cell with *c* = 107.509(2) Å.

**Table** Atomic coordinates for the Mo9Ge16 compound
(space group *I*4122 (#98), Pearson symbol *tI*100, *a* = 5.99324(3), *c* = 44.0005(3) Å

|  |  |  |  |
| --- | --- | --- | --- |
| Atom | Wyckoffposition | Atomic coordinates | *B*iso (Å2) |
| *x* | *y* | *z* |
| Mo1 | 4*a* | 0 | 0 | 0 | 0.65(2) |
| Mo2 | 8*c* | 0 | 0 | 0.7763(1) | 0.66(2) |
| Mo3 | 8*c* | 0 | 0 | 0.4463(1) | 0.64(2) |
| Mo4 | 8*c* | 0 | 0 | 0.66837(9) | 0.59(2) |
| Mo5 | 8*c* | 0 | 0 | 0.1108(2) | 0.59(2) |
| Ge1 | 8*f* | 0.348(1) | 1/4 | 1/8 | 0.75(2) |
| Ge2 | 8*d* | 0.3389(7) | 0.3389(7) | 0 | 0.69(2) |
| Ge3 | 16*g* | 0.3163(6) | 0.8507(7) | 0.03095(8) | 0.78(2) |
| Ge4 | 16*g* | 0.2268(5) | 0.6481(7) | 0.09242(8) | 0.80(2) |
| Ge5 | 16*g* | 0.1498(6) | 0.1789(5) | 0.05893(6) | 0.68(2) |

#### [1] Völlenkle, H. (1967). *Z. Kristallogr*. **124**, 9-25.

#### [2] Rohrer, F. E., Lind, H., Eriksson, L., Larsson, A. K. & Lidin, S. (2000). *Z. Kristallogr*. **215**, 650-660.

#### [3] Yamamoto, A. (1993) *Acta Crystallogr*. **49**, 831-846.