Representatives of the Nowotny Chimney-Ladder phases in the Mo–Ge system

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In the binary system Mo–Ge, the existence of the compound $Mo_{13}Ge_{23}$ 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 c_T and c_M, 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 $K\alpha_1$ radiation).

Two compounds were observed: Mo_9Ge_{16} (space group $I4_122$, Pearson symbol *tI*100, *a* = 5.99324(3), *c* = 44.0005(3) Å and $Mo_{22}Ge_{39}$, (*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 Mo_9Ge_{16} 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 Mo_9Ge_{16} compound are given in the table below. The structure of the $Mo_{22}Ge_{39}$ 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 Mo_9Ge_{16} compound
(space group $I4_122$ (#98), Pearson symbol *tI*100, *a* = 5.99324(3), *c* = 44.0005(3) Å

Atom	Wyckoff position	Atomic coordinates			B_{iso} (Å^2)
		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.