Eur. J. Mineral.
2009, **21**, 863–869
Published online August 2009

OD (order-disorder) character of the crystal structure of godlevskite Ni_9S_8

STEFANO MERLINO[1,*] and EMIL MAKOVICKY[2]

[1] Department of Earth Science, University of Pisa, Via S. Maria 53, 56126 Pisa, Italy
*Corresponding author, e-mail: merlino@dst.unipi.it
[2] Department of Geography and Geology, University of Copenhagen, Østervoldgade 10, 1350 Copenhagen, Denmark

Abstract: Godlevskite Ni_9S_8 has been found to be an OD (order-disorder) structure consisting of two kinds of OD layers in strict alternation; these layers display stacking disorder. They have layer symmetries $P(\overline{4})2m$ and $P2_12(2)$, respectively (symmetry elements in parentheses are perpendicular to OD layers). Two structures with maximum degree of order (MDO polytypes), with space-group symmetries $A222$ and $I4_122$, respectively, exist, together with more complex polytypes or disordered sequences. The OD character is in keeping with the frequent twinning of godlevskite.

Key-words: godlevskite, nickel arsenide, OD structure, polytypes.

1. Introduction

The crystal structure of godlevskite was described by Fleet (1987, 1988) as a structure with statistically occupied positions and frequent twinning. This suggested us a possible occurrence of OD phenomena in this structure, interesting also because the OD phenomena are present in another nickel-rich ore mineral, maucherite $Ni_{11}As_8$ (Fleet, 1973; Makovicky & Merlino, 2009). These phases came to our attention while studying crystal chemistry of chalcogenides and pnictides of platinum-group elements and cations of the 8th group in general (Makovicky, 2006).

Godlevskite, Ni_9S_8, is typical of the lower-temperature associations of nickel sulphide deposits with sulphur fugacities below those required for millerite, NiS. It is one of the nickel-excess sulphides known, the others being heazlewoodite, Ni_3S_2 (Parise, 1980), and synthetic α-Ni_7S_6 (Fleet, 1972). Their phase relations and chemical compositions have been clarified by Fleet (1988). The structures of all these phases, as well as that of millerite, β-NiS (Grice & Ferguson, 1974), are distinguished by the presence of numerous direct Ni-Ni interactions. In spite of similar stoichiometry, the crystal structure of godlevskite differs profoundly from that of cubic pentlandite, $(Ni,Fe)_9S_8$ (Rajamani & Prewitt, 1974).

Godlevskite, maucherite and the above recalled Ni-excess sulphides are important examples of crystal-chemical characteristics of nickel in its chalcogenides/pnictides – specific coordination polyhedra, metal–metal interactions and deviations from Pauling's principle of parsimony. Palladium does not form these structure types, revealing subtle but important differences in the crystal chemistry of these two elements. Phase studies (Karup-Møller & Makovicky, 1993) indicate that in the temperature range 550 °C–400 °C the above indicated phases all display only a very low solubility of palladium, in contradiction to the behaviour of $Ni_{1-x}S$ and $Ni_{3\pm x}S_2$ that are stable at higher temperatures.

Structure data were obtained from the Inorganic Crystal Structure Database (2006).

2. Crystal structure of godlevskite

The structure of godlevskite has been determined and refined by Fleet (1987) as orthorhombic, space group $C222$, $a = 9.3359$ Å, $b = 11.2185$ Å, $c = 9.4300$ Å, $Z = 4$. Crystals studied were complexly twinned (Fleet, 1987, 1988). The structure can be described as a sphalerite-like packing of NiS_4 coordination tetrahedra with numerous vacancies in which the tetrahedra are replaced by square coordination pyramids NiS_5. Fig. 1 shows alternation of (001) layers of tetrahedra (horizontal) that contain additional, interstitial NiS_4 tetrahedra (rendered in ball-and-stick presentation, coloured black) and some square coordination pyramids, with tetrahedral layers of another kind, that are rich in square coordination pyramids (ball-and-stick, white presentation). The short Ni–Ni contacts are not illustrated.

The structure may be interpreted on the basis of OD theory of structures built up by distinct types of layer.

0935-1221/09/0021-1961 $ 3.15
DOI: 10.1127/0935-1221/2009/0021-1961