MISFIT LAYER COMPOUNDS $(MS)_nTS_2$ (M = Sn, Pb, Bi, RARE EARTH ; T = Nb, Ta ; n = 1.08/1.19) ; A NEW CLASS OF LAYER STRUCTURE

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We recently found that compounds with the assumed "MTS_3" composition are mixed layer structures with real $(MS)_nTS_2$ composition. Indeed they are built up of alternately double layers of MS and sandwiches TS_2. To illustrate that structural type we will refer to the structural determinations of $(SnS)_{1.17}NbS_2$ (1) and $(LaS)_{1.14}NbS_2$ (2). The former structure has been solved by taking into account separate sublattices SnS and NbS_2 in a composite approach, while the second one has been treated as a supercell, in a commensurate approximation.

I - STRUCTURE OF $(SnS)_{1.17}NbS_2$

The structure determination of this compound has been split up in three parts :

i) SnS part using hkl reflections ($h \neq o$) in an orthorhombic unit cell with dimensions a_1 = 5.763 Å, b_1 = 5.750 Å, c_1 = 11.76 Å, space group Cm2a, Z = 4.

ii) NbS_2 part using hkl reflections ($h \neq o$) in an orthorhombic unit cell with dimensions : a_2 = 3.321 Å, b_2 = 5.750 Å, c_2 = 11.76 Å, space group Cm2m, Z = 2.

iii) The relative origin (shift along the b axes) was found from the projection along [100] using okl reflections common to the SnS and NbS_2. The sublattices of the SnS and NbS_2 structure match along the b and c axes, but not along the a axes, the ratio being a_1/a_2 = 5.763/3.321 = 1.708. The composition of the crystal $(SnS)_{1.17}NbS_2$ is determined by the misfit ratio (1.17 = 2/1.708).

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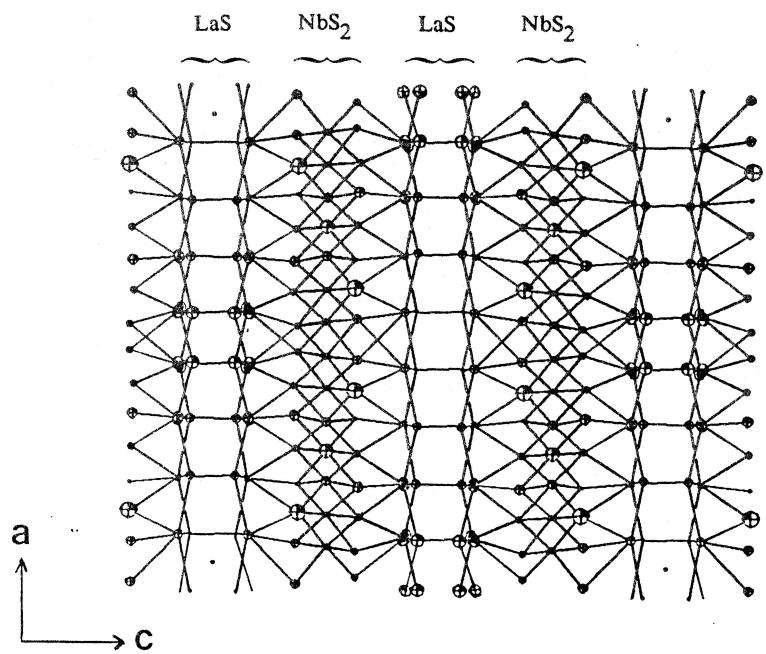
II - STRUCTURE OF $(LaS)_{1.14}NbS_2$

The structure determination has been conducted in a supercell approach with unit cell dimensions : a = 23.216 Å, b = 5.806 Å, c = 23.031 Å.

The first analysis (2) was done with the centrosymmetric Bbcb space group which led to a bad R factor (R = 0.155). The structure investigation through a composite approach (3) as already discussed for $(SnS)_{1.17}NbS_2$ showed that LaS part with a' = a/4, b" = b, c' = c/2, S.G. Cm2a and NbS_2 part with a" = a/7, b' = b, c" = c, S.G. Fm2m yielded to a better solution as R factors are as low as 0.048 and 0.087 respectively for LaS and NbS_2 parts, and to 0.067 for the okl reflections common to both sublattices.

The supercell approach can be easily refound from these results. Its space group is obtained as the maximal common subgroup of the subsystem space groups. Among three possible space groups $Bm2_1b$, Bb2b or B11b, our choice was focussed on the Bb2b non centrosymmetric one.

Then, another investigation of the structure was undertaken (4). This time, a much better solution is obtained since the R factor converged to a value of 0.067 for 830 hkl (94 variables). This is quite reasonable since incommensurability remains ignored (see fig). The analysis or the R factors shows homogeneous results even for the weakest reflections corresponding to the satellite ones originating from the mutual modulation.



III - PHYSICAL PROPERTIES

All the "MTS_3" compounds studied by resistivity measurements indicate a metallic behavior even at low temperature (2,5,6). it is observed that the resistivity is strongly anisotropic with a ratio of $\rho_{//c}/\rho_{\perp c}$ of about 10^5 at 4K, $\rho_{\perp c}$ being the in-plane resistivity (5,6).

Some of these compounds were known for a long time for their superconducting transition at very low temperature (e.g., $PbNbS_3$ and $PbTaS_3$ at T_c~2.65K and 3.11K, respectively) (7,8). But at that time neither their structure nor their exact chemical formulation were known. The origin of the superconducting transition was referred to the presence of the TS_2 slab (T_c of NbS_2 and TaS_2 at 6K and 2K, respectively).

From Hall measurements it was deduced that this kind of compounds compensate their valence charge in a way that the MS part acts as donor, the TS_2 part as an acceptor (5,6).

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