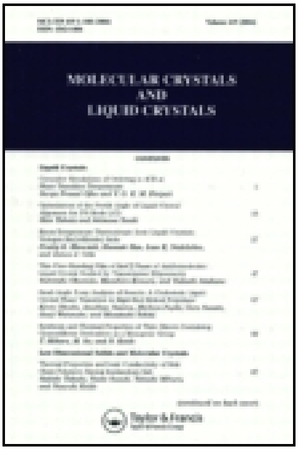


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Misfit Layer Compounds $(MX)_n(TX_2)_m$ [M= Sn,Pb,Bi,Rare Earth; T= Transition Metal; X=S,Se; 1.08<n<1.25; m=1,2]

Jean Rouxel [a] & Alain Meerschaut [a]
[a] I.M.N., Laboratoire de Chimie des Solides, U.M.R. 110, C.N.R.S., Université de Nantes, 2 rue de la Houssinière, 44072, Nantes cedex 03, France

Version of record first published: 23 Oct 2006.

To cite this article: Jean Rouxel & Alain Meerschaut (1994): Misfit Layer Compounds $(MX)_n(TX_2)_m$ [M= Sn,Pb,Bi,Rare Earth; T= Transition Metal; X=S,Se; 1.08<n<1.25; m=1,2], Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 343-354

To link to this article: http://dx.doi.org/10.1080/10587259408050128

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 343–354
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

MISFIT LAYER COMPOUNDS $(MX)_n(TX_2)_m$ [M= Sn,Pb,Bi,Rare Earth;T= Transition Metal; X=S,Se; 1.08<n<1.25; m=1,2]

Jean ROUXEL and Alain MEERSCHAUT

I.M.N., Laboratoire de Chimie des Solides, U.M.R. 110, C.N.R.S.,
Université de Nantes, 2 rue de la Houssinière,
44072 Nantes cedex 03, France.

Abstract The misfit layered compounds $(MX)_n$ $(TX_2)_m$ with M= Sn, Pb, Bi, Ln; T= Ti, V, Cr, Nb, Ta; X= S, Se; m= 1, 2 result from an alternate stacking of NaCl like MX slabs and TX_2 sandwiches. The in-plane a parameters of both sublattices are incommensurate, hence the structural misfit and complicated formulations like $(LaS)_{1.14}NbS_2$. In the case of M= Ln there is a partial electronic transfer from MX to TX_2 which leads to consider these phases as infinite two-dimensional intercalation compounds. Some of the compounds are highly anisotropic superconductors, all have very striking physical properties. An interplay between MX and TX_2 layers allow to vary the number of each of them. In the case of the bilayer compounds $(MX)_n(TX_2)_2$ it is possible to practice "second order" intercalation reactions between successive TX_2 layers.

INTRODUCTION

What is a misfit structure? The so-called misfit structures can be described as two or more interpenetrating sublattices with periods that are commensurate in some directions but incommensurate in others ,i.e., the ratio of the two periodicities in the incommensurate direction is an irrational number. Compounds with misfit stuctures are broken into two classes, semi-commensurate phases when the two periodicities comprise a ratio of two small integers (7/4,12/7,13/12 for example) and incommensurate phases for all other cases (irrational fractions or ratio of very large integers, these being eventually very close to each other)(1). The primary importance of this distinction lies in the idea that the semi-commensurate periodicity ratios may suggest a case of a "lock in" of the two layers. The term "vernier structure" has been applied to these structures. In a single vernier structure the component layers contain n and n+1 subcells, respectively. In higher order vernier structures these multiples are n and n+p, respectively where p is the order (see figure 1).

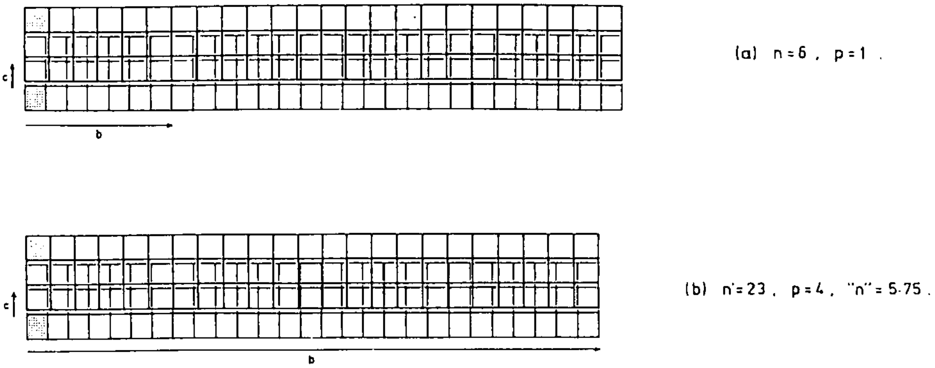


FIGURE 1 - Hypothetical SC layer structures with modulation along [010]. The two subcells are shown slightly displaced along [001]; (a) a unit vernier; (b) a multiple vernier of order p (after Makovicky and Hyde, ref.(1)).

A one-dimensional misfit structure is usually composed of separate columns (or channels) of different kinds. For example, $Eu_{1-x}Cr_2X_{4-x}$ (X= S,Se; x=0.29) compounds described by BROUWER and JELLINEK (2) have a channel type structure. They refer to an intergrowth of three types of structural units which have a common hexagonal basal plane, but different and mutually incommensurate c axes. The framework formed by CrX_6 octahedra sharing edges and faces, leaves wide channels around the threefold and sixfold axes. These channels are filled respectively with Eu_3X and $Eu_6Cr_2X_6$ chains with different repeat periods along the chain direction.

In the layered misfit structures two different slabs alternate regularly along the stacking direction. The misfit between the layers arises from the difference in size and /or orientation of the layer nets. The in-plane non-commensurability can be observed in one or two directions. One of the first misfit layered compound to be mentioned is the $FeCl_3$-graphite intercalated compound described by COWLEY and IBERS in 1956 (3).

To these one or two-dimensional structures one can add what is referred to as an overgrowth structures. An overgrowth structure contains monolayers adsorbed on a substrate like gold on silicon, noble gas monolayers on graphite....Electronic superlattices can also be regarded with the same concepts.

DESCRIPTION OF MISFIT LAYER STRUCTURES

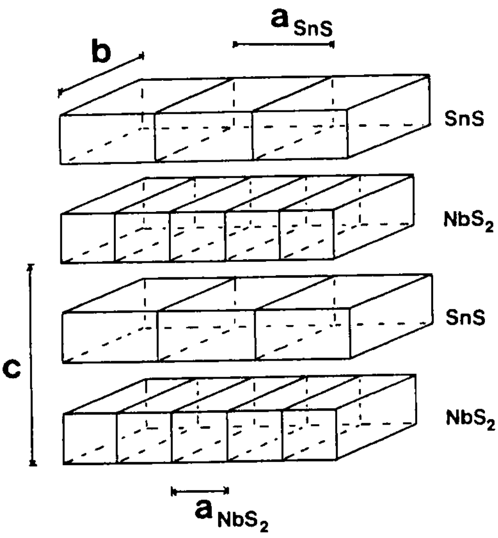


FIGURE 2 - The structure of $(SnS)_{1.17}NbS_2$ [based on SnS and NbS_2 building units] (after Wiegers et al (4)).

The structure of misfit layered chalcogenides can be described on the basis of an alternating sequence of MX slabs and TX_2 sandwiches along the c direction. The MX unit has a deformed NaCl structural type arrangement. The TX_2 unit exhibits a structural type similar to that observed for binary layered TX_2 compounds; the sandwiches have octahedral coordination of T when T= Ti, V, Cr but trigonal prismatic one when T= Nb,Ta. Each unit has its own "in-plane" **a** and **b** parameters. The **b** parameters for the two sublattices are identical while the **a** parameters are different with an irrational ratio (misfit)(figure 2)(4).

This ratio also determines the chemical formulation ($n= 2a_{TX2}/a_{MX}$); for example, $(LaS)_{1.20}CrS_2$, $(PbS)_{1.18}TiS_2$, $(PbS)_{1.13}VS_2$, $(SnS)_{1.17}NbS_2$....

These compounds can be prepared in evacuated quartz ampoules using either the elements or the binary compounds at temperatures of 900 to 1100°C. Another way which is successful is treating the corresponding ternary oxides under CS_2 or H_2S vapor at 1300-1400°C. This is very convenient for rare earth derivatives: for example, sulfurization of $LnCrO_3$ leads directly to misfit compounds. Nice platelet-shaped single crystals are obtained when iodine is used as transport agent.

CHEMICAL BONDS

Understanding the chemical bonding in the misfit layered compounds is difficult. One has to separate compounds with MX subpart when M= rare earth element from those with M= Sn, Pb, Bi. A very important point is that the latter compounds do not exist for the CrS_2 counter part. This has certainly to do with the stability of TX_2 slabs and provides an interesting first indication about bonds in the misfit phases.

Let us consider the band structure that can be associated to TS_2 slabs. Between a valence band that is essentially a ligand sp in character and antibonding levels that originate mostly from the corresponding cationic sp levels, the d orbitals of the metal, split by the crystal field, play an essential role in determining the physical properties. Additionally, they govern the stability, and even the stoichiometries, of layered structures. In the presence of sulfur, the metal has the maximum oxidation state of four, leading to d^0 configuration and no electronic conductivity in the case of group IVA elements. The octahedral environment of the metal results in a broad , empty t_{2g} conduction band. For V, Nb, and Ta, a d^1 configuration leads to the lower symmetry trigonal prismatic coordination. The associated band structure is composed of a narrow a'_1 band below the e' and e" bands. The a'_1, mostly comprised of metal dz^2 orbitals, is lower in energy than the t_{2g}. The result is a net stabilization and metallic behavior. Next, MoS_2 and WS_2 which have a d^2 configuration and trigonal prismatic symmetry are diamagnetic semiconductors. Further to the right, a return to octahedral symmetry for layered MnS_2 is expected (no stabilization through a trigonal prismatic distortion for a d^3 configuration), but that phase cannot be obtained. In fact, for metals further to the right of the periodic table, the d levels are progressively lower in energy and overlap with the sp valence band. Under such conditions, empty d levels are filled at the expense of the valence band, at the top of which holes appear (see figures 3). In other words, the cation is reduced and the anion is oxidized via the formation of anionic pairs. As a result, layered structures (such as TiS_2, with Ti^{4+} and $2S^{2-}$) becomes pyrites and marcasites (with Fe^{2+} and $(S_2)^{2-}$, for example) (for a critical discussion see for example references (5,6))..

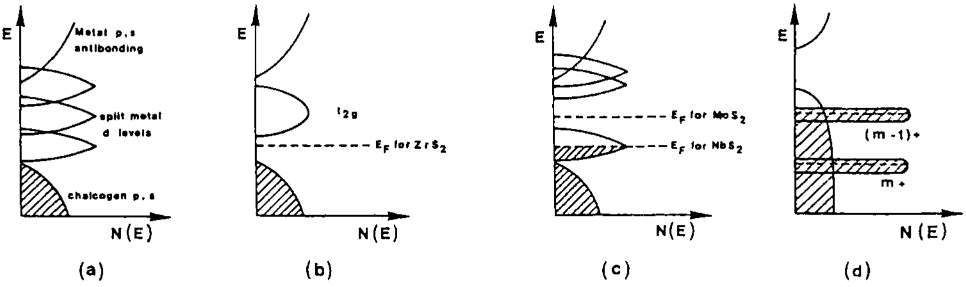


FIGURE 3 - Simplified band models for layered chalcogenides: (a) general scheme; (b) octahedral slabs; (c) trigonal prismatic slabs; (d) cationic levels and sp anionic band at the end of a period.

One can play with the relative position of d bands and sp bands. Because selenium is less electronegative than sulfur, the top of the sp valence band in metal diselenides is situated at a higher level, and such a transition is observed earlier in selenides relative to sulfides. Now, with a more electropositive cations, d levels are pushed up and layered structures are stabilized. This is the case for the elements at the bottom of a column. MoS_2 and WS_2 have layered structures but a layered CrS_2 compound is unknown. Cr^{4+} is unstable in the presence of sulfur. However, there is a $NaCrS_2$ phase which is structurally similar to the $NaTiS_2$ intercalation compound (α $NaFeO_2$ structural type).. Chromium has been reduced to Cr^{3+}, d^3 configuration, and we have the expected octahedral MS_2 slabs. But the sp band is filled up (semiconducting properties). Indeed, Na has given one electron to the top of the sp band and prevents the formation of anionic pairs. This filling of the sp band stabilizes the layered arrangement. We observed such a stabilization for Si_xCrSe_2 (7) or P_xVS_2 (8). This fact strongly suggests that in $(LnS)_nCrS_2$ phases (with CrS_2 octahedral slabs), the LnS part would transfer electrons to the CrS_2 layers. This is likely due to the electronic structure of Ln^{3+} e^- S^{2-} of rare earth monochalcogenides. The electron lies in a broad 5d band for the first rare earth elements of the period leading to metallic properties. Then 4f levels become more stable and such a narrow band leads to a metal-non metal Mott type transition. What we would have here is a partial or total transfer of this electron to the TS_2 part. This should not occur in the case of SnS or PbS. Such a scheme has been clearly established by electrical transport properties (resistivity, Hall coefficient and Seebeck coefficient)(9). Misfit layered compounds can then be viewed as infinite two-dimensional intercalation compounds.

What happens on intercalating the transition metal chalcogenides? The rigid band model assumes that the shape of the band structure of the dichalcogenide is not changed on intercalation, the only change being a filling of the conduction band with the valence electrons from the intercalated metal. One may suppose the model to be correct for alkali metal intercalates with Coulomb type interaction between the alkali metal ion and the negatively charged sandwich layers of TS_2, the valence electron being donated to the dz^2 conduction band. Physical properties of the intercalates, the alkali as well as the more covalent 3d transition metal compounds, are in first approximation in agreement with the rigid band model (10).

MULTILAYER MISFIT COMPOUNDS: POLTYPISM.

We have been able to prepare new series of misfit compounds in which the MX slabs are separated by a group of two TX_2 slabs (11,12,13). Examples are $(PbS)_{1.18}(TiS_2)_2$ (14), $(PbS)_{1.14}(NbS_2)_2$ [orthorhombic and monoclinic symmetries] (15,16), $(PbSe)_{1.12}(NbSe_2)_2$ (17), $(LaSe)_{1.14}(NbSe_2)_2$ (18). For TiS_2 derivatives the structural type showed a normal stacking of the TiS_2 slabs, as found in pure TiS_2 itself (1T form)(see figure 4).

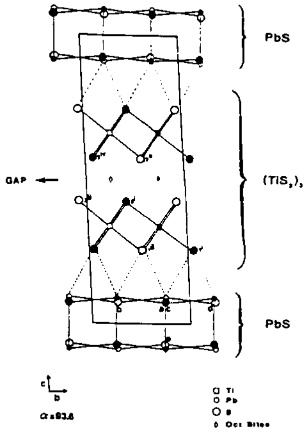


FIGURE 4 - Projection of the structure of $(PbS)_{1.18}(TiS_2)_2$ along

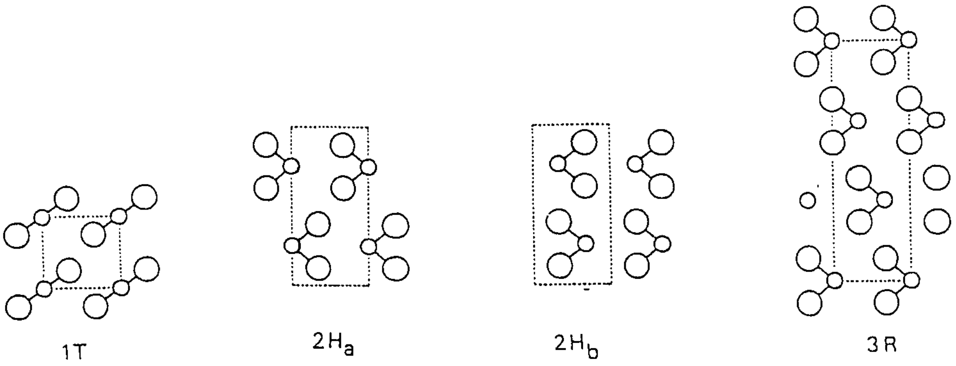


FIGURE 5 - some polytypes observed in layer-type MX_2 compounds

For pure NbX_2 compounds polytypes can be found. The most commonly observed polymorphs are of 2H and 3R types (see figure 5). They correspond to two or three successive NbX_2 slabs (in the stacking direction), respectively. A 2H stacking mode was expected in the double slabs misfit compounds. Indeed, this is observed in the selenide derivatives (see figures 6a and 6b).

However, a 3R stacking mode (2/3 of 3R in fact) is found for the sulfide derivatives (15,16). We will see later on the importance of the stacking mode of NbX_2 slabs versus the superconducting properties.

As mentioned above, two polymorphs of $(PbS)_{1.14}(NbS_2)_2$ have been identified (orthorhombic and monoclinic symmetry)(see figures 7a and 7b).. For the monoclinic form, the structure refinement led to a partial population of the octahedral sites in the van der Waals gap (vdW) with extra-niobium atoms. The chemical formulation appears as $(PbS)_{1.14}(Nb_{1.049}S_2)_2$ or $(PbS)_{1.14}[Nb_{0.098}(NbS_2)_2]$(16). These additional Nb atoms are not located exactly at the center of the octahedral arrangement of sulfur. They are shifted from this center to minimize Nb-Nb repulsion with Nb atoms of the adjacent NbS_2 slabs. This results in unequivalent Nb-S distances (three short and three long) but nearly equivalent Nb-Nb bond lengths.

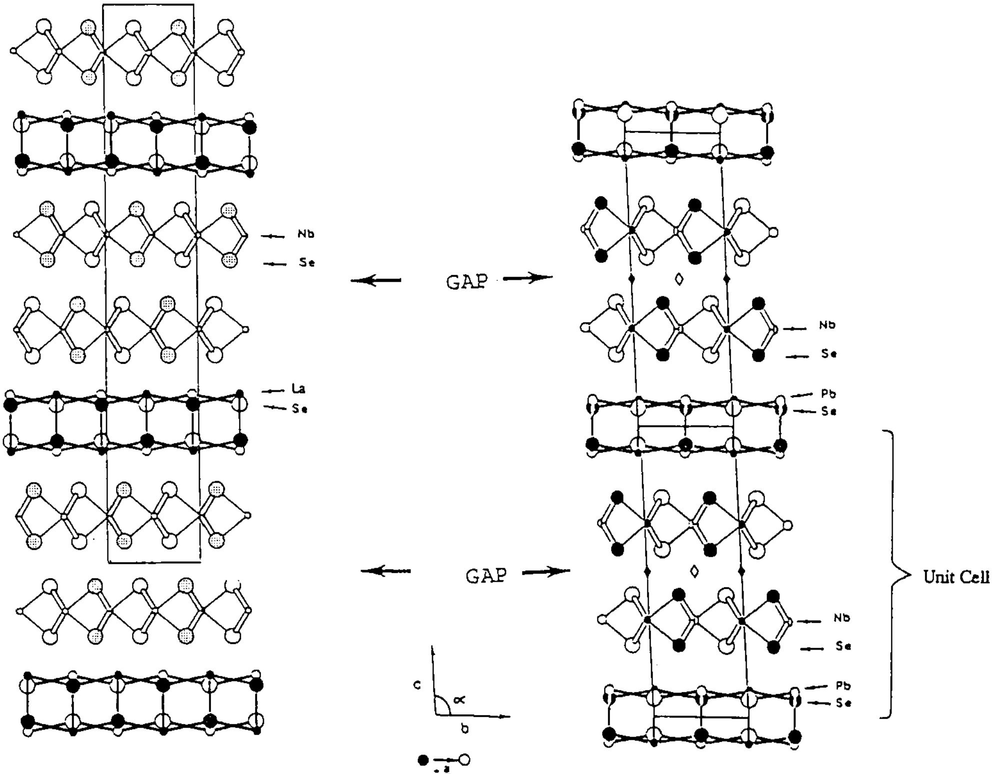
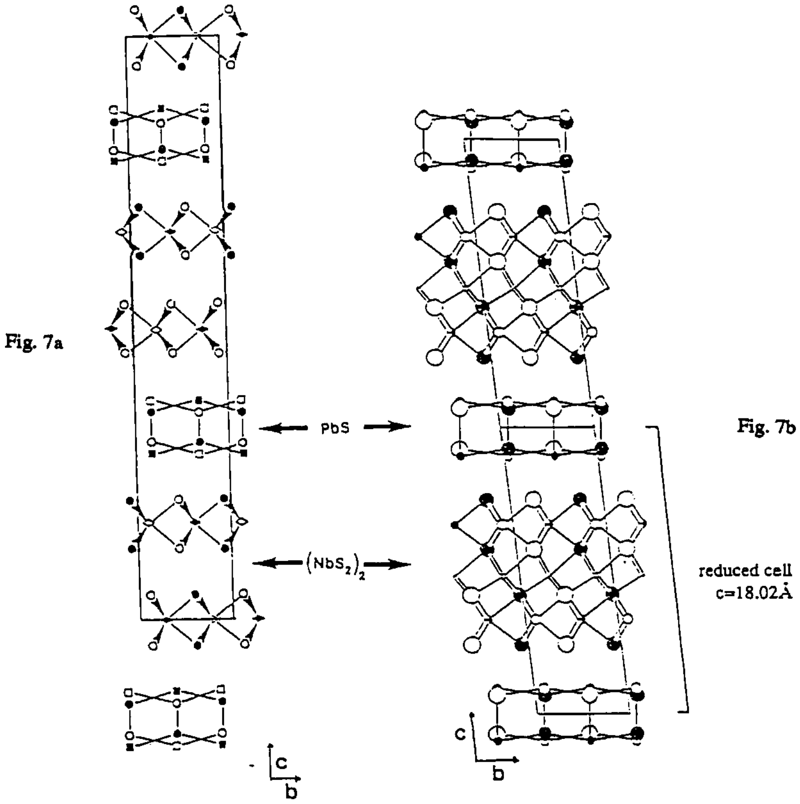


Fig. 6a

Fig. 6b

FIGURES 6 a,b - Projection of the structure along the misfit axis; (a) "$LaNb_2Se_5$"; (b) "$PbNb_2Se_5$"

The presence of extra-niobium atoms within the vdW gap recalls us the intercalated M_xNbS_2 phases (M= Ti, V, Cr, Mn, Fe..) which, for the smallest x values referred to the 3R stacking mode of NbS_2 slabs (19). Here, the 3R organization corresponds to a non-stoichiometry within the NbS_2 part as observed in the pure $Nb_{1+x}S_2$ binary compounds (20). It is "a self intercalation compound". Perhaps, a higher amount of extra-atoms could be reached with ordered occupancies when x=0.25 and 0.33.



FIGURES 7 a,b - Projection of the structure of $(PbS)_{1.14}(NbS_2)_2$: (a) orthorhombic form; (b) monoclinic form

The orthorhombic form which also exhibits a 3R stacking mode of the NbS_2 slabs differs from the monoclinic form in the orientation of NbS_2 blocks along c. These blocks have an altemated orientation in the orthorhombic case but not for the monoclinic one. No additional Nb atoms within the vdW gap is found for the orthorhombic form (figure 7a)

Due to the presence of a vdW gap (between àdjacent TX_2 sandwiches) for the misfit bilayer compounds, it can be anticipated that they will be useful as host lattices for intercalation chemistry, like the transition metal dichalcogenides themselves. This can provide a convenient way to change the electronic properties of these phases. For example, figure 8 shows the discharge curve corresponding to the intercalation of lithium into "$PbNb_2S_5$" (21,22). An abrupt decrease in the voltage is observed above 0.96 Li content. It can be assumed that Li atoms occupy first the vacant octahedral sites on the basis of size considerations (see figure 9); moreover, Li atoms are generally octahedrally coordinated with sulfur. The increase of the c parameter upon Li intercalation (see figure 10) is comparable to what is found in the Li-TX_2 systems (10).

In the absence of reliable X-rays spectra above x=0.96 (Li), it is not possible to ascertain the role of lithium.

In pure NbS_2 it is difficult to reach the limit x = 1 Li, although there is one octahedral site available per NbS_2 in the vdW gap. Indeed, electronic considerations are limiting the process. At the same time electrons are added to the dz^2 band. Strong repulsions in a narrow band already half filled can explain the difficulty of filling all the octahedral sites. Here we are filling the octahedral sites too, but two slabs are involved in electronic transfer.

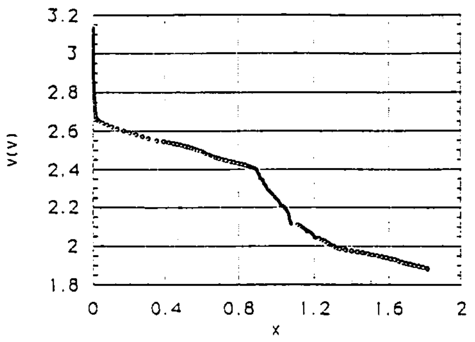


FIGURE 8 - Potentiostatic discharge curve V= f(x_{Li})

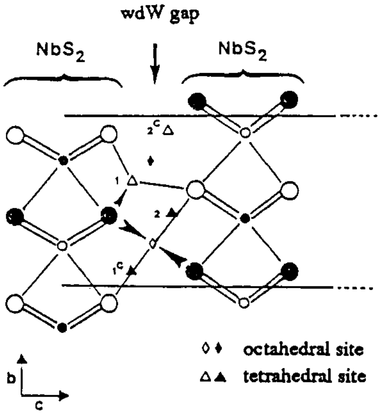


FIGURE 9 - Octahedral (◊) and tetrahedral (Δ) sites

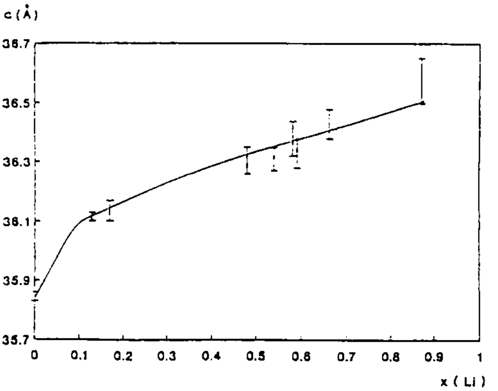


FIGURE 10 - variation of the C(Å) parameter versus X_{Li}

ELECTRICAL TRANSPORT PROPERTIES.

The misfit layered compounds show a wide range of very interesting properties, most of them still being under investigation.

First it is worth noting that these compounds have excellent lubricating properties which is an interesting fact since they are thermally more stable than MoS_2. Compounds with NbS_2, TaS_2, TiS_2 slabs show metallic conductivity with conduction most likely related with the TX_2 part. Lanthanide misfit derivatives bring two-dimensional magnetic properties which can exist solely in the LnX part or associated with the TX_2 part when T= Cr. As a large variety of MX entities are existing it should be possible to prepare solid solutions with M and M' elements of different nature; in that way, a dilution of magnetic elements (Ln^{3+}) with non-magnetic ones such as Sn^{2+} will be of interest. This example allows Mossbauer studies; this substitution will also modify the quantity of the electronic transfer from MX to TX_2 parts.

The resistivity versus temperature plots do not show anomalies which can be attributed to CDW' type transitions as found in some binary TX_2 compounds. This indicates that the Fermi surface does not have the nesting properties of the pristine dichalcogenides, which may be due to the mutual modulation between both subparts. This modulation causes strongly distorted coordination of X around T, compared to the already orthorhombically distorted average structures. The resistivity along c, ρ_c , is much higher than the in-plane resistivity for all the compounds. The ratio ρ_{ab}/ρ_c is as small as 10^{-4}. This anisotropy is also much higher for the misfit than for the pure homologue TX_2 compounds (10^2-10^3)(9). Compounds with M= Pb, Bi, Sn, La can be superconductors. For example, "$LaNb_2Se_5$" undergoes a superconducting phase transition (18) at T_c= 5.3K (see figure 11). The critical temperature is lower than the one observed in pure $NbSe_2$ (T_c= 7.2K), but higher than in the "monolayer $LaNbSe_3$" (Tc ≈ 2 K) (24). When increasing the number of $NbSe_2$ slabs one gets closer to the value of pure $NbSe_2$.

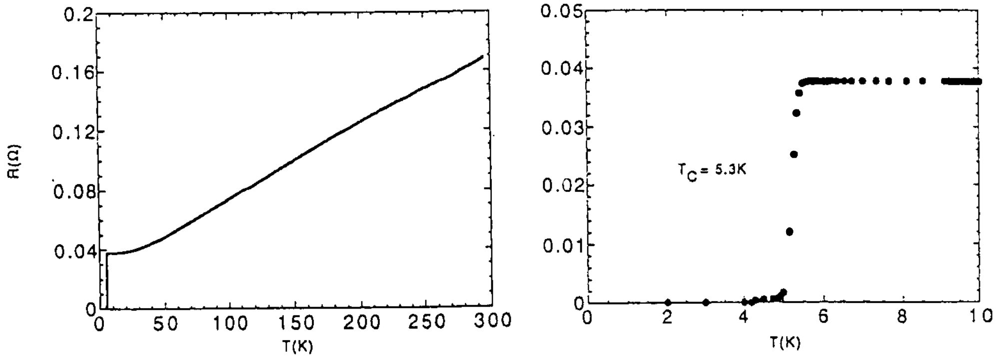


FIGURE 11 - Variation of resistance of "$LaNb_2Se_5$" as a function of temperature

The type of stacking mode appears to play an important role on the occurrence/or not of the superconducting transition. Thus, in "$LaNb_2Se_5$" the stacking mode is $2H_a$ as in $2H_a$-$NbSe_2$; both compounds are superconductors. However, "$PbNb_2S_5$" with a 3R type stacking mode is not a superconductor and neither is 3R-NbS_2. On the contrary 2H-NbS_2 is a superconductor (25) (T_c = 6K) and consequently the presence or absence of superconducting properties in polytypes of NbS_2 was supposed to be related to the stacking mode since the same local symmetry and the same electronic structure are observed. The misfit compounds seem to confirm this point.

The Hall coefficient (R_H) is positive for all investigated compounds (monolayers only), indicating hole conduction; the Hall coefficient increases when going from 300 to 4K. The Seebeck coefficient (α) is negative for compounds with M= Sn, Pb and Bi, but positive for lanthanides derivatives (9). For the latter, one may assume that the conduction is by holes only as both R_H and α are positive. When R_H and α are of opposite signs a two carrier mechanism is occurring, viz., by light holes (small effective mass) which determine the positive sign of the Hall coefficient and by heavy electrons (large effective mass) which determine the (negative) sign of α.

The properties of the misfit compounds with M= Sn, Pb, Bi, are quite similar to those of the silver intercalates Ag_xTS_2 (T= Nb, Ta) viz., a positive Hall coefficient corresponding with only a slight donation of electrons to the conduction band and a negative Seebeck coefficient (26,27). Therefore, the electronic properties were attributed to conduction in the $4dz^2$ ($5dz^2$) band of the NbS_2 (TaS_2) parts of the structures. The number of holes/T calculated from R_H assuming that only holes contribute, are in favor for a slight donation of MX to TX_2. For the lanthanides derivatives, the properties are in agreement with an almost complete filled dz^2 conduction band of the NbS_2 (TaS_2) parts.

ACKNOWLEDGMENTS

This research was supported by the French government (MRT- contract n° 90 A 785) and the European Community (CEE- programme Science, n° SC1-0496 C). We appreciated the fruiful cooperation with Pr. G.A. WIEGERS and his coworkers (laboratory of Inorganic Chemistry, University of Groningen - The Netherlands).

REFERENCES

1. E. Mackovicky and B.G. Hyde, Structure bonding, 46, 101 (1981).
2. R. Brouwer and F. Jellinek, Journal de Physique Coll., 38, C7 (1977).
3. J.M. Cowley and J.A. Ibers, Acta Cryst. 9, 421 (1956).
4. G.A. Wiegers, A. Meetsma, S. van Smaalen, R.J. Haange, J. Wulff, T. Zeinstra, J.L. de Boer, S. Kuypers, G. van Tendeloo, J. van Landuyt, S. Amelinckx, A. Meerschaut, P. Rabu and J. Rouxel, Sol. State Comm., 70(4), 409 (1989).
5. F. Jellinek, Inorg. Sulfur Chem., G. Nickless Ed., Elsevier (1968).
6. S. Jobic, R. Brec and J. Rouxel, Journal of Alloys and Compds., 178, 253 (1992).
7. D. Odink, G. Ouvrard and J. Rouxel, unpublished results.

8. R. Brec, G. Ouvrard, R. Freour, J. Rouxel and J.L. Soubeyroux, Mat. Res. Bull., 18, 689 (1983).

9. G.A. Wiegers and A. Meerschaut, in Incommensurate Sandwiched Layered Compounds, edited by A. Meerschaut (Materials Science Forum 100-101),Chap. 2, 101 (1992).

10. W.R. Mac Kinnon, in Chemical Physics of Intercalation, edited by A.P. Legrand and S. Flandrois (NATO Asi Series B, 172, 181 (1987).

11. L. Guemas, P. Rabu, A. Meerschaut and J. Rouxel, Mat. Res. Bull., 23, 1061 (1988).

12. Y. Oosawa, Y. Gotoh, J. Akimoto, T. Tsunoda, M. Sohma and M. Onoda, Jpn. J. Appl. Phys. 31, 11096 (1992).

13. Y. Oosawa, Y. Gotoh and M. Onoda, Chemistry Letters, 1563 (1989).

14. A. Meerschaut, C. Auriel and J. Rouxel, Journal of Alloys and Compds., 183, 129 (1992).

15. A. Meerschaut, L. Guemas, C. Auriel and J. Rouxel, Eur. J. Solid State Inorg. Chem., 27, 557 (1990).

16. C. Auriel, A. Meerschaut and J. Rouxel, Mat. Res. Bull., submitted (1993).

17. C. Auriel, A. Meerschaut, R. Roesky and J. Rouxel, Eur. J. Solid State Inorg. Chem., 29, 1079 (1992).

18. R. Roesky, A. Meerschaut, J. Rouxel and J. Chen, Z. Anorg. Allg. Chem., 619, 117 (1993).

19. J. Rouxel, A. Leblanc and A. Royer, Bull. Soc. Chim. Fr., 6, 2019 (1971).

20. F. Kadijk and F. Jellinek, J. Less Common Met., 19, 421 (1969).

21. C. Auriel, A. Meerschaut, P. Deniard and J. Rouxel, C.R. Acad. Sci. Paris, t313, 1255 (1991).

22. L. Hernan, J. Morales, L. Sanchez and J.L. Tirado, Solid State Ionics, 58, 179 (1992).

23. L. Hernan, J. Morales, J. Pattanayak and J.L. Tirado, J. of Solid St. Chem., 100, 262 (1992).

24. R. Roesky, A. Meerschaut, J. Rouxel, J. Chen and P. Monceau, unpublished results.

25. W.G. Fisher, Univ. Thesis, Cornell (USA) (1978.

26. H.J.M. Bouwmeester, A. van der Lee, S. van Smaalen, G.A. Wiegers, Phys. Rev. B43, 9431 (1991).

27. A. Diedering, R.H. Haange and G.A. Wiegers, unpublished results.