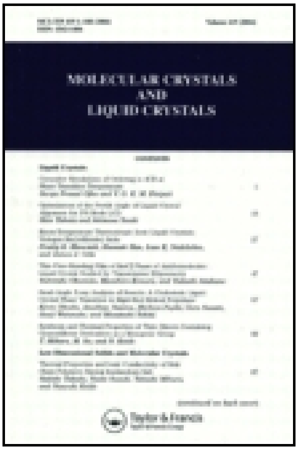

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Origin of Structural Instability in Layered Intercalation Compounds

Vladislav S. Pervov [a] , Elena V. Makhonina [a] & Vladislav V. Volkov [a]

[a] Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 117907, Russia

Version of record first published: 27 Oct 2006

To cite this article: Vladislav S. Pervov, Elena V. Makhonina & Vladislav V. Volkov (2000): Origin of Structural Instability in Layered Intercalation Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 131-136

To link to this article: http://dx.doi.org/10.1080/10587250008026129

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 131-136
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Origin of Structural Instability in Layered Intercalation Compounds

VLADISLAV S. PERVOV, ELENA V. MAKHONINA
and VLADISLAV V. VOLKOV

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 117907 Russia

The mechanisms of the phase transitions in the A_aMX_2-type intercalates (A-metal, MX_2- layered dichalcogenide matrix) occurring upon a change in the stoichiometry (a) are studied. It is shown that maximal stoichiometric ratios, and trends of structural changes in intercalates are determined by stabilization of conduction bands ("electronic stabilization") of intercalates.

Keywords: layered dichalcogenides; stoichiometry of intercalation compounds; structural stability

The formation and some properties (including structural changes) of the A_aMX_2 intercalates (A = metal, MX_2 = layered dichalcogenide matrix of the 2H-MoS_2 structural type) at various concentrations (a) were studied by X-ray powder diffraction analysis, electron diffraction studies, high resolution electron microscopy, scanning electron microscopy, energy dispersive X-ray, microprobe elemental analysis, mass-spectrometry, and electrophysical, electrochemical and magnetic measurements. Using the synthetic matrices $Ta_{1-x}Re_xS_{2-y}Se_y$ (**TRX**) allowed us to regulate the filling of the conduction bands on retention of the structure of the 2H-MoS_2 type.

The structure of the synthesized matrix $Ta_{0.5}Re_{0.5}Se_2$ (**TRS**) was studied in detail[1]. It was shown that a small change in the Ta/Re ratio locally disturbing the electronic stabilization led to the formation of structure defects. The defect structure of **TRS** is characterized by the presence of a number of rotation twins.

A self-consistent structure-physical model for the coexistence of R-twins, 2D-defects and prismatic cluster defects in the material was proposed[11]. The analysis of the **TRS** microstructure led to explanation of its excellent lubricant properties and the role of defect interfaces as microstructure in this process.

A comparison study of the intercalates A_aMoX_2 (X = S, Se) and of the intercalates based on the synthetic matrix $A_aTa_{0.5}Re_{0.5}S_{2-y}Se_y$ (A = Sn, In, Ga, Fe, Co, Ni, Li; a = 0.25-0.5, y = 0.6-2.0) was carried out. The intercalates were synthesized by ampule technique at high temperature and, in the case of A = Li, by electrochemical intercalation. The complex synthetic matrices, on the one hand, and molybdenum dichalcogenides, on the other hand, differently behave in the course of intercalation. The layered intercalates of MoS_2 and $MoSe_2$ with Fe, Co, and Ni are not obtained. In the case of A = Ga, a structural transition from the layered molybdenum dichalcogenide to a spinel structure is observed. Under the same conditions, the intercalation with Fe, Co, and Ni seems to lead to the disproportionation of the complex matrices **TRX** according to the following scheme (exemplified by $Ta_{0.5}Re_{0.5}Se_2$):

$$A_a + Ta_{0.5}Re_{0.5}Se_2 = A_bTa_zSe_{2z} + A_{a-b}Ta_{0.5-z}Re_{0.5}Se_{2-2z} \qquad (1)$$

The 2-H $TaSe_2$ and 2-H $NbSe_2$ matrices were intercalated with gallium. The products of composition Ga_aMSe_2 (a = 0.25, 0.33, 0.5; M = Ta, Nb) were prepared from high purity elements in evacuated sealed quartz tubes at 800°C. In synthesis, the M/Se ratio was varied. The synthesis was carried out for 100 h in four steps. After each 25-h annealing, the samples were quenched and examined. It was found that the phases with a spinel structure and gallium monoselenide were formed at the first stage, independently of the composition. The equilibrium was achieved after annealing for 75 h. For both Ta and Nb, the final compound in the mixture with the composition $Ga_{0.5}MSe_2$ was a single phase with a spinel structure (needle-shaped), and the final products in the mixtures having compositions $Ga_{0.25}MSe_2$ and $Ga_{0.33}MSe_2$ consisted of two phases (with spinel and hexagonal structures).

The electron microscopy and microprobe elemental analysis data show that the hexagonal crystals are the intercalates of tentative composition Ga_aMS_2 (a = 0.1-0.15). To determine the gallium concentration (a) in the Ga_aMSe_2 intercalates in the equilibrium $GaSe–Ga_xM_2Se_4–Ga_aMSe_2$ system more precisely, the synthesis from MS_2 (placed separately) and a $GaSe–Ga_xM_2Se_4$ mixture (as a feed of Ga) was carried out with the use of GaI_3 as a transporting agent. The concentration a in Ga_aMSe_2 was determined from the change in weight of the initial MS_2 and the final product and by X-ray diffraction analysis and was found to be a = 0.12 ± 0.05.

The X-ray powder diffraction patterns of the needle-shaped crystals (table) reveal the additional reflections characteristic of the ordered structures of the $Ga_xV_yM_4Se_8$ type (space group 4F3m, Z = 4, V - lattice vacancy).

TABLE X-ray powder pattern of $Ga_{0.50}TaSe_2$

d, Å	*I*, % after 1-st, 2-d, 3-d, and 4-th annealing (separated by comma)	*hkl*
5.86	35, 36, 18, 36	111
5.10	9, 7, 5, 5	200
3.68	3, 1, 5, 6	220
3.10	31, 42, 59, 60	311
2.57	100, 100, 83, 99	400
2.36	12, 24, 31, 36	331
2.10	35, 32, 75, 81	422
1.82	42, 52, 100, 100	440
1.49	0.1, 12, 30, 33	444
1.44	0.2, 13, 42, 42	711
1.38	0, 15, 56, 55	642
1.34	0, 13, 55, 55	731
1.29	0.5, 7, 17, 18	800
1.21	0.5, 28, 72, 70	751

It can be assumed that these crystals are formed by the following multistep reaction (for M = Nb):

$$Ga(0) + bNbSe2 \rightarrow GaSe + Nb_bSe_{2b-1}V_{se} \qquad (2)$$

$$Nb_bSe_{2b-1}V_{se} \rightarrow Nb_4Se_7V_{se} \qquad \text{(e.g., for b = 4)} \qquad (3)$$

$$GaSe + Nb_4Se_7V_{se} \rightarrow GaNb_4Se_8 \qquad (4)$$

It was found that an excess of selenium (relative to stoichiometry) resulted in instability of spinel phases:

$$2Ga_xV_yNb_4Se_8 + 3xSe \rightarrow xGa_2Se_3 + 8NbSe_2 \qquad (5)$$

To discuss a possibility for these reactions to occur, we should take into account the common structural features of the intercalation compounds A_aMX_2 and the spinels AM_2X_4. To a first approximation, the crystal structure of spinel along the C_3 axis (the body diagonal of the cubic unit cell) can be viewed as a sequence of $X\text{–}M_{1-\delta}\text{–}X$ layers separated by $A_{0.25}\text{–}M_\delta\text{–}A'_{0.25}$ cation layers, where A and A' are cations in positions 4_a and 4_c, respectively, of the ordered spinel structure. Therefore, the cation layers can be viewed as a result of ordering of intercalated ions. The changes in the anion surrounding of M ions (from trigonal-prismatic coordination in the layered structure to pseudooctahedral coordination in the ordered spinel structure) can be interpreted as due to an in-plane displacement in the chalcogen layers by $1/2[1\ 1\ \bar{2}]$. The charge transfer from Ga atoms partly reduces M (Ta or Nb).

The measurements of magnetic susceptibility of $Ga_{0.5}TaSe_2$ showed that this compound exhibited weak paramagnetism: the effective magnetic moment decreased from 0.56×10^{-23} J/T at room temperature to 0.31×10^{-23} J/T at 79 K; magnetic susceptibility increased in this temperature range by 8% and did not obey the Curie–Weiss law (figure). The magnetic behavior of $Ga_{0.5}TaSe_2$ was interpreted in the assumption of the formation of tetrahedral clusters Ta_4 with localized unpaired electrons (as in $Ga_{0.5}Mo_2S_4$[12]). A reduction in the magnetic moment per Ta_4 cluster (as compared with the spin-only value for one unpaired electron) and its decrease with decreasing temperature may be explained by antiferromagnetic exchange between the localized electrons.

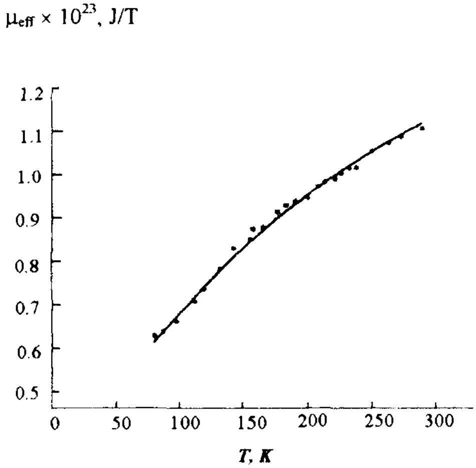

FIGURE 2 The effective magnetic moment in $Ga_{0.50}TaSe_2$ vs. temperature; the solid line shows the best fit curve obtained in the model of exchange between infinite chains.

Therefore, two mechanisms of conduction band stabilization can be responsible for the structural transformation from layered intercalates of the Ga_xMSe_2 type to the spinel structure. According to the first mechanism, a gain in energy is expected to be due to changes in the anion environment of M ions (from trigonal-prismatic in the layered structure to pseudooctahedral coordination in the spinel structure) and, thus, to an increase in occupancy of t_{2g} orbitals. An additional gain in energy is expected to be caused by formation of metal-metal bonds in the M_4 clusters, resulting in the removing of the degeneracy of t_{2g} orbitals in the octahedral environment of metal atoms. The concept of electronic stabilization, as applied to the problem of structural stability of layered dichalcogenide matrices upon intercalation, is complicated by the fact that the valences of atoms forming the conduction bands are uncertain.

Acknowledgments

The authors thank Prof. J. Van Landuyt and Prof. S. Amelinckx for helpful discussions and for their help with the structure study of the **TRS** matrix. This work was supported by the Russian Foundation for Basic Research, projects no. 96-03-033170 and 99-03-32550a.

References

[1] V. V. Volkov, J. Van Landuyt, S. Amelinckx, V. S. Pervov, and E. V. Makhonina, *J. Solid State Chem.*, **135,** 235 (1998).
[2] J. M. Vanderberg and D. Brasen, *J. Solid State Chem.*, **14,** 203 (1975).