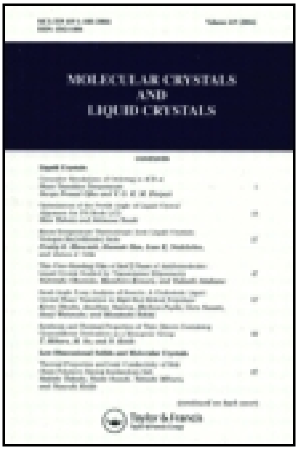


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Charge Transfer in Misfit Layer Chalcogenides, $[(MX)^n]^{1+x}(TX^2)^m$: a Key for Understanding their Stability and Properties

A. Meerschaut [a], Y. Moëlo [a], L. Cario [a], A. Lafond [a] & C. Deudon [a]
[a] Institut des Matériaux Jean Rouxel, UMR-CNRS 6502, Université de Nantes, Lab. de Chimie des Solides, 2 rue de la Houssiniére, 44322, Nantes, France

To cite this article: A. Meerschaut, Y. Moëlo, L. Cario, A. Lafond & C. Deudon (2000): Charge Transfer in Misfit Layer Chalcogenides, $[(MX)^n]^{1+x}(TX^2)^m$: a Key for Understanding their Stability and Properties, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 1-8

To link to this article: http://dx.doi.org/10.1080/10587250008026108

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 1-8
Reprints available directly from the publisher
Photocopying permitted by license only

Charge Transfer in Misfit Layer Chalcogenides, $[(MX)_n]_{1+x}(TX_2)_m$: a Key for Understanding their Stability and Properties

A. MEERSCHAUT, Y. MOËLO, L. CARIO, A. LAFOND
and C. DEUDON

Institut des Matériaux Jean Rouxel, UMR-CNRS 6502, Université de Nantes, Lab. de Chimie des Solides, 2 rue de la Houssinière, 44322 Nantes, France

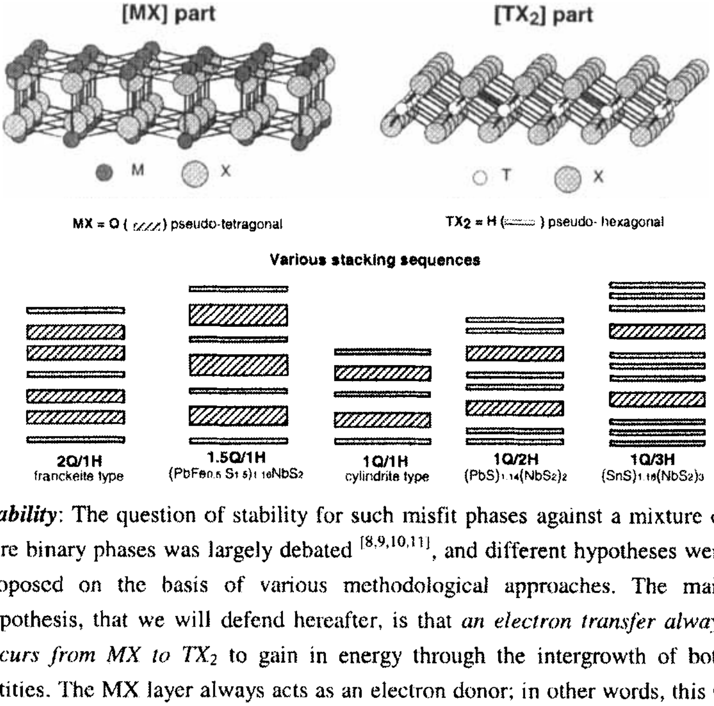
Stability of misfit layer chalcogenides (M.L.C.) is always governed by a charge transfer (C.T.) mechanism. A comparison between M.L.C. and parent intercalated layered binary systems shows comparable characteristics, which illustrate the role of electron donor for the MX part (or its corresponding A-intercalant species) towards the TX_2 acceptor part. In that way, intercalation chemistry within the vdW gap of multilayered TX_2 misfit derivatives is also considered. The donor character of the MX part, easy to understand when trivalent M cations are present, can be also assumed if a divalent M cation is partly substituted for a trivalent one, as revealed from precise electron microprobe analysis. Examples of M.L.C. with enlarged MX part (with mixed M^{+II}, M^{+III}) emphasize the reality of the C.T.. This M-to-T donor effect necessarily controls the transport and intercalation properties.

Keywords: misfit layer chalcogenide; charge transfer; intercalation

INTRODUCTION

Definition: In the last decade, many new synthetic ternary chalcogenides showing a 2D-composite structure and belonging to the family of incommensurate compounds, namely ***the misfit layer compounds (MLC)***, were reported in the literature [1,2].They can be formulated as $[(MX)_n]_{1+x}(TX)_m$ (M = rare earth, Sn, Pb, Bi, Sb...; T = Ti, V, Cr, Nb, Ta; X = S, Se; $n = 1, 1.5, 2$ and $m = 1, 2, 3$, with $1.08 < 1+x < 1.28$). The building principle of their structures consists of an alternate stacking of two layered sets, namely MX and TX_2 (see Fig.). Incommensurability comes from the inequality of periodicities between the two components, along the *a*-direction; the ratio a_H/a_Q is generally irrational, with $(1+x) = 2\ a_H/a_Q$. The stacking sequence is related to the *n/m* ratio.The early MLC corresponded to the simplest homologue (*n* & *m* = 1:

"monolayer type"). Later on, "multilayer types" (n = 1, m = 2 or 3) were reported [3,4,5], with one (m = 2) or two (m = 3) van der Waals (vdW) gaps in the H-part. Recently, an opposite situation was encountered in which m = 1 but n = 1.5 [6] or 2 [7].



Stability: The question of stability for such misfit phases against a mixture of pure binary phases was largely debated [8,9,10,11], and different hypotheses were proposed on the basis of various methodological approaches. The main hypothesis, that we will defend hereafter, is that *an electron transfer always occurs from MX to* TX_2 to gain in energy through the intergrowth of both entities. The MX layer always acts as an electron donor; in other words, this Q layer can be considered as *a 2D-intercalate (positively charged) inside a* TX_2 *host compound.* In addition to the resulting charge transfer (C.T.) from the Q-part, a further C.T. can occur in "multilayer types" through intercalation of cations (atoms or molecules) in the v.d.W. gaps.

1- INTERCALATION IN THE V.D.W. GAP OF MULTILAYER TYPES

1.1- Intercalation with alkaline metals

Most of intercalation studies into multilayer types were performed by Tirado & coll. [12]. Chemical (with n-butyllithium or sodium naphtalide solution in THF) as well as electrochemical techniques showed that the intercalation of Li or Na takes place topotactically. For Na, the upper intercalation limit approaches one atom per bilayer unit formula (i.e. ≈0.5 e^-/T), indicating the filling of vacant octahedral sites [12c]. A higher degree of intercalation is reported for Li (but below 2 at. / unit formula [12a], i.e. 1 e^-/T), which implies tetrahedral site occupancy too. Alkali incorporation at the Q/H interface cannot be envisioned, since no significant intercalation has been observed in the monolayer type ($m = 1$). So, it appears that the C.T. upper limit of alkali intercalation is essentially governed by steric aspects, and not electronic ones: indeed, the complete filling of the T-dz^2 conduction band, in accordance with the rigid band model, of 1 e^-/T (T in trigonal prismatic coordination) is never reached.

1.2 – Intercalation of organic molecules

Various organic molecules (e.g., cobaltocene [13]) have been intercalated in multilayer compounds, but not in the (1Q, 1H) corresponding homologues, that confirms the specific role of the v.d.W. gap. The *c*-expansion value resulting from intercalation of identical species in either dichalcogenides or misfit host structures is comparable, but generally smaller than expected from the v.d.W. dimension of the molecule. This can be easily explained by the ionization of the guest species upon intercalation, with consequently a donor effect. Nevertheless, the cobaltocene content per transition metal is lowered relatively to parent binary compounds; this has to be related with the pre-existing donor effect from the MX part (see below), even if no significant change in the binding energies of all the elements (metal and chalcogen) was evidenced from a comparison of XPS results for non-intercalated ternary (misfit) and binary chalcogenides [13].

1.3 – Intercalation with transition metals

First of all, one must point out that, like in pristine dichalcogenides, a limited *auto-intercalation* of T atoms (i.e. Nb, Ti) within the v.d.W. gap is frequently encountered among multilayer types. Occurrence of specific polytypes is determined by such an auto-intercalation process; this is well known for the 3R-stacking mode in NbS_2 [14] and Pb misfit derivatives [15]. In M.L.C., the auto-intercalation site occupancy factor (s.o.f.) is around 10 %, which leads to a maximum possible C.T. of ~ 0.25 e^-/T.

Intercalation of other transition metals was recently performed with Cu [16], Fe or Ni [17]. Thus, the bilayer type $[MS]_{1+x}$ $[(NbS_2)_2Cu_y]$, with M = Ce, Sm and $y = 0.67$ (at the maximum uptake), was ascertained, and its electronic structure studied by means of XPS and EELS spectroscopies [16]. Cu atoms were assumed to occupy one-third of the two available tetrahedral sites per Nb atom (for $y = 0.67$). A phase transition takes place and would correspond to a change from the trigonal prismatic coordination of Nb atoms (at lowest Cu-content) to the octahedral one (at the highest Cu-content). As XPS results indicate monovalent copper, the Cu C.T. is ~ 0.33 e^-/T.

Fe-intercalated bilayer misfit phases have also been obtained [17]. A very recent collaboration with Suzuki & coll. was engaged for the crystal structure determination of $[LaS]_{1.14}[(NbS_2)_2Fe_{0.33}]$. Preliminary results are undoubtedly in favor of the $2H_a$-NbS_2 stacking type for adjacent NbS_2 layers (i.e. Nb in a trigonal prismatic coordination with intercalated Fe in octahedral one). Although there are two times less Fe- than Cu-intercalated atoms, the result in terms of the Nb d_{z^2} band filling is identical either with 0.33 Fe^{2+} or 0.67 Cu^+. Thus, the change of coordination from trigonal prismatic to octahedral proposed above for Cu, but unobserved for Fe, ought to be verified by X-ray crystal structure determination.

2- THE MX LAYER ACTING AS A 2D-INTERCALATE

2.1 – Total charge transfer with trivalent cations : the case of LnS/CrS$_2$

Evidence of a C.T. when the M element is a trivalent cation (e.g., rare earth metal (Ln), Sb, Bi...) is easy to accept, for instance for Ln/Cr M.L.C. It is well known that Cr^{4+} is not stable with chalcogen atoms, which excludes the formation of a layered binary CrS_2 compound. But such a CrS_2 slab is observed in the ternary $ACrS_2$ compounds (A = Li, Na), where A is the electron donating species opposite to the acceptor CrS_2 part; CrS_2 layers are also observed in M.L.C when they are interstacked with LnS layers. In both situations, chromium has been reduced to Cr^{3+} ions. On the contrary, existence of misfit chromium derivatives was not reported with a divalent M element (e.g., Sn, Pb) because of no transfer. This is an indirect proof in favor of a strict C.T. of 1e^-/Cr atom.

The expected valence states for chromium (Cr^{3+}) and lanthanum (La^{3+}) are confirmed by magnetic measurements [18]. All the $(LnS)_{1+x}CrS_2$ compounds (Ln = La...Yb) are semiconductors [19]; this could be rather surprising because, once the C.T. of 1e^-/Cr is achieved, an excess of x e^- should remain in the LnS slab, i.e., delocalized in the 5d band, leading then to an (unobserved) metallic conductivity. Chemical analysis with Castaing electron microprobe (EPM) of the M.L.C. with supposed $(GdS)_{1.27}CrS_2$ formula indicated it to be actually $(Gd_{0.91}\square_{0.09}S)_{1.27}CrS_2$ ($\square$ = vacancy on the Gd sites) [20]. This leads to an exact charge balance for Gd^{3+}, Cr^{3+} and S^{2-}. Consequently, *no excess electrons exist and the observed semiconducting behavior is now explained.*

The presence of vacancies thus appears as a direct consequence of electronic considerations, namely a strict trivalent state for Ln and Cr. But one can suppress these vacancies through an appropriate cationic substitution, performed at a constant C.T. ($1e^-$/Cr); this is illustrated for instance in ~$LaCrS_3$ with Sr^{2+} substituting for La^{3+} in proportion of $2La^{3+} + \square \leftrightarrow 3Sr^{2+}$. The starting La-deficiency is $(La_{0.94}\square_{0.06}S)_{1.2}CrS_2$, better expressed as $(LaS)^{1+}(La_{2/3}\square_{1/3}S)^0_{0.2}(CrS_2)^{1-}$; Sr substitution up to a complete filling of vacancies leads to $(LaS)^{1+}(SrS)^0_{0.20}(CrS_2)^{1-}$. Any intermediate situation is represented by the general formulation $(LaS)(La_{2/3(1-y)}\square_{1/3(1-y)}Sr_yS)_{0.2}CrS_2$, with $0 \leq y \leq 1$ [21]. Refinement of (La,Sr)S subcell parameters for y = 0.0, 0.25, 0.50, 0.75 and 1 gives a quasi-linear increase of the *c*-parameter ($r_{(La^{3+})} = 1.03$ Å $< r_{(Sr^{2+})} = 1.18$ Å), which confirms that substitution is operating up to $y = 1$. As expected, the synthesis of an oversubstituted $(La_{0.9}Sr_{0.3}S_{1.2})CrS_2$ compound failed. Band structure calculations (TB-LMTO-ASA method) of $(LaS)(SrS)_{0.20}CrS_2$ (commensurate approximation $5\ a_{(CrS_2)} = 3\ a_{(LaS)}$) were compared with those obtained for the hypothetical isolated (La,Sr)S and CrS_2 layers [21]. The most significant difference is the shift of the (La,Sr)S part towards higher energies when both layers are combined (i.e., in M.L.C.). The band structure of this M.L.C can be regarded approximately as a superposition of the band structures of the two components (except the adjustement of the Fermi levels); the interlayer cohesion in this misfit is due to ionic interactions between La of the (La,Sr)S part and S atoms of the CrS_2 one.

La/Sr substitution was also considered for the V-sulfide M.L.C.. Nishikawa and coll.[22] studied the transport properties of $La_{1.17-x}Sr_xVS_{3.17}$; they observed that the carrier concentration in the VS_2 layers is changed with x, because of the interlayer C.T. mechanism. Thus, a Mott-type metal-insulator transition is realized in this M.L.C., the insulating state being achieved for $x = 0.17$, while a metallic state takes place for $x > 0.3$.

2.2 – Hidden C.T. with a divalent cation: the case of (Pb,Sn)S/TS$_2$

C.T. was questioned for a divalent cation (Pb, Sn), because Q- and H-layers alone apparently respect an electron neutrality. On the basis of various spectroscopic methods (UPS, XPS, XAS...), Ohno [8,23] and Hangyo *et al.* [24], claimed that C.T. occurs even for divalent M, but at a lower level than for trivalent M cation. On the contrary, considering same physical approaches, Ettema *et al.* [9] considered that C.T. is small (if it exists!) and not sufficient to explain the stability of the MLC with a divalent M metal atom.

This question was cleared up by EPM performed for the series of M.L.C $(M^{2+}S)_{1+x}(T^{4+}S_2)_m$, with M = Sn, Pb; T = Ti, Nb; *m* = 1, 2, 3 [25]. When the Q- and H-slabs were considered to have the ideal stoichiometric compositions MS and TS$_2$ respectively, EPM reveals a systematic shift towards higher T/M ratios. This is explained as a partial substitution (≈10 at.%) of T for M in the MS slab, as realized by such an heterovalent substitution rule: $M_Q^{2+} + T_H^{4+} \rightarrow T_Q^{3+} + T_H^{3+}$ (with equal amount of T_Q^{3+} and T_H^{3+} - "cationic coupling"). Presence of tri- (or tetravalent ?) Ti or Nb cations substituted for divalent Sn or Pb within the MS slab necessary induces a C.T. towards the TS$_2$ slab (d_z^2 band filling). According to this T-for-M substitution the general chemical formula of these M.L.C. thus becomes $[(M_{1-y}T_y)S]_{1+x}$ $[(TS_2)_mT_z^*]$ with $y \sim 0.1$ (* plus $z \sim 0.09$ for polytypes with interstitial T cations).

2.3 – Intermediate charge transfer: stabilization of new homologues

Two new compounds related to the stacking type $n = 1.5$ and $m = 1$, with chemical formulations $[(Pb_{2/3}Fe_{1/3}S)_{1.5}]_{1.16}[NbS_2]$ [6b] and $[(EuS)_{1.5}]_{1.15}$ $[NbS_2]$ [6a] were recently obtained. In the first compound the Q-part consists of a sandwich of two PbS planes confining a central FeS one, with Fe^{3+} (according to ^{57}Fe Mössbauer results and bond valence calculations). In the Eu-derivative the Q-slab is built up from three EuS planes, with the central metal atom in an octahedral coordination ; Mössbauer and magnetic measurements indicate a mixed-valency for Eu [26]: +III for central Eu, and +II for Eu at the margins. Thus, in these two new M.L.C., the C.T. from the Q-part is ensured by the presence of Fe^{3+} or Eu^{3+} (~ 0.58 e^-/Nb).

The M.L.C. homologue corresponding to the stacking type $n = 2$ and $m = 1$ is illustrated by the synthesis of the franckeite-type compound with composition $[(Pb_{1-y}Sb_yS)_2]_{1.14}NbS_2$ ($y \sim 0.2$) [7]. Here, the four-atom-thick

Q-layer is stabilized by the stereochemical activity of Sb^{3+} cations, with the C.T. of ~ 0.45 e^-/Nb due to Sb^{3+}.

3- CHARGE TRANSFER: A GUIDE FOR THE RE-INTERPRETATION OF CHEMICAL AND PHYSICAL PROPERTIES AMONG M.L.C.

As far as electron transfer is concerned, this should have an impact on transport properties. One of the most convenient way to quantify this electron donation is to perform Hall (coupled with Seebeck) measurements. Indeed, on the basis of the rigid band model, electron donation from MX to TX_2 part must decrease the number of holes in the $d_z{}^2$ band of T = Nb, Ta. Wiegers [2] reported many results for the monolayer type with di- and trivalent M cations. All these results are in favor of an electron transfer, as deduced from $R_H = -1/(ne)$, with the $d_z{}^2$ band of Nb (Ta) almost filled (~ 0.1 hole/T, that is C.T. ~ 0.9 e^-/T) in case of a trivalent M cation (rare earth metal). A much less transfer was found for divalent cations (Sn, Pb), for instance around 0.87 h/Nb according to Hall effect in $(SnS)_{1.17}NbS_2$, which has a *p*-type metallic electronic conduction [11], even if the calculated amount is not very reliable for a situation close to a half-filled band. A band-structure calculation on this Sn-derivative performed by Fang et al. [11] indicates a small transfer of about 0.4 e^-/Nb. On the basis of XPS, XAS and EELS studies, Ohno [27] also concluded about the existence of C.T.

Vibrational studies [23, 28] and optical studies [29,30] gave no conclusive results about C.T. with divalent M cations. Thus, from optical data, Rüscher et al. [28] found no significant C.T. for a divalent M cation (Pb), but a strong C.T. when a trivalent cation (La, Sm, Tb) is involved. Some other results from XPS experiments [9], also gave conclusion of a small or absent C.T. for divalent M.

Clearly, this long controversy about C.T. for divalent M cations has no more grounds to be debated, once one takes into account the actual chemical composition of M.L.C., with T-for-M substitution. C.T. is the main stabilizing factor for M.L.C., and necessitates a precise knowledge of their crystal chemistry. Exact significance of transport or chemical properties are conditioned by high quality requirements for synthesis and crystal chemical characterization of M.L.C.

References

[1] G.A. Wiegers and A. Meerschaut, in *Materials Science Forum*, edited by A. Meerschaut (Trans Tech Publications Ltd, Aedermannsdorf, 1992), Chap. 2, p. 101.

[2] G.A. Wiegers, in *Prog. Solid St. Chem.* (Elsevier Science Ltd, 1996) **24,** p. 1.

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

[4] Y. Oosawa, Y. Gotoh, J. Akimoto, T. Tsunoda, M. Sohma and M. Onoda, *Jpn.J. Appl. Phys.*, **31,** L 1096 (1992).

[5] L.M. Hoistad, A. Meerschaut, P. Bonneau and J. Rouxel, *J. Solid State Chem.*, **114,** 435 (1995).

[6] a- L. Cario, A. Meerschaut, C. Deudon and J. Rouxel, *C.R. Acad.Sci. Paris,* **1 série IIc,** 269 (1998).
b- A. Lafond, C. Deudon, A. Meerschaut, P. Palvadeau, Y. Moelo and A. Briggs, *J. Solid State Chem.*, **142,** 461 (1999).

[7] A. Lafond, A. Nader, Y. Moelo, A. Meerschaut, A.Briggs, S. Perrin, P. Monceau and J. Rouxel, *J. Alloys and Compds.*, **261,** 114 (1997).

[8] Y. Ohno, *Solid State Comm.*, **79**(12), 1081 (1991).

[9] A.R.H.F. Ettema and C. Haas, *J. Phys.: Condens. Matter,* **5,** 3817 (1993).

[10] A. Meerschaut, Current Opinion in *Solid State&Materials Science*, edited by C.N.R. Rao and J. Rouxel, (1996), 1(2), p.250.

[11] C.M. Fang, A.R.H.F. Ettema, C. Haas, G.A. Wiegers, H. van Leuken and R.A. de Groot, *Phys. Rev. B,* **52**(4), 2336 (1995).

[12] a- L. Hernan, J. Morales, J. Pattanayak and J.L. Tirado, *J. Solid State Chem.,* **100,** 262 (1992).
b- C. Barriga, P. Lavela, J. Morales, J. Pattanayak and J.L. Tirado, *Chem. Mater.,* **4,** 1021 (1992).
c- L. Hernan, J. Morales, L. Sanchez and J.L. Tirado, *Solid State Ionics* **58,** 179 (1992).

[13] L. Hernan, J. Morales, L. Sanchez, J.L. Tirado, J.P. Espinos and A.R. Gonzalez Elipe, *Chem. Mater.,* **7,** 1576 (1995).

[14] W.G. Fischer and M.J. Sienko, *Inorg.Chem.* **19,** 39 (1980).

[15] C. Auriel, A. Meerschaut and J. Rouxel, *Mat. Res. Bull.* **28,** 675 (1993).

[16] Y. Ohno, *J. Solid State Chem.*, **134,** 99 (1997).

[17] K. Suzuki, O. Nakamura, T. Kondo and T. Enoki, *J. Phys. Chem Solids,* **6–8,** 1133 (1996).

[18] A. Lafond, A. Meerschaut, J. Rouxel, J.L. Tholence and A. Sulpice, *Phys. Rev. B* **52**(2), 1112 (1995).

[19] P.G. Rustamov, T.Kh. Kurbanov, O.M. Aliev. I.P. Aliev, G.G. Guseinov and M.A. Alidzhanov, *Izv. Akad. Nauk. SSSR Neorg. Mater.*, **16**(5), 811 (1980).

[20] J. Rouxel, Y. Moëlo, A. Lafond, F.J. DiSalvo, A. Meerschaut and R. Roesky, *Inorg. Chem.*, **33,** 3358 (1994).

[21] L. Cario, D. Johrendt, A. Lafond, C. Felser, A. Meerschaut and J. Rouxel, *Phys. Rev. B* **55**(15), 9409 (1997).

[22] T. Nishikawa, Y. Yasui and M. Sato, *J. Phys. Soc. Japan,* **63**(9), 3218 (1994).

[23] Y. Ohno, *Phys. Rev. B* **48**(8), 5515 (1993).

[24] M. Hangyo, T. Nishio, S. Nakashima, Y. Ohno, T. Terashima and N. Kojima, *Jpn. J. Appl. Phys.*, **32–3,** 581 (1993).

[25] Y. Moëlo, A. Meerschaut, J. Rouxel and C. Auriel, *Chem. Mater.,* **7,** 1759 (1995).

[26] L. Cario, A. Lafond, P. Palvadeau, C. Deudon and A. Meerschaut, *J. Solid State Chem.,*accepted (1999).

[27] Y. Ohno, *Phys.Rev. B* **44** (3), 1281 (1991).

[28] C. Sourisseau, R. Cavagnat and J.L. Tirado, *Raman Spectrosc.*, **23,** 647 (1992).

[29] C.H. Rüscher, C. Haas, S. van Smaalen and G.A. Wiegers, *J. Phys., Condens. Matter,* **6,** 2117 (1994).

[30] R. Roesky, P. Gressier, A. Meerschaut, K. Widder, H.P. Geserich and G. Scheiber, *J. Phys.: Condens. Matter,* **6,** 3437 (1994).