ELSEVIER

Journal of Alloys and Compounds 262-263 (1997) 406-409

Journal of ALLOYS AND COMPOUNDS

Superconducting and structural properties of rare-earth-based Chevrel-phase selenides $REMo_6Se_8$: first single crystal studies

F. Le Berre[a], O. Peña[a,*], C. Hamard[a], R. Horyń[b], A. Wojakowski[b]

[a] *Chimie du Solide et Inorganique Moléculaire, CSIM-UMR 6511, Université de Rennes I, 35042 Rennes Cedex, France*
[b] *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50950 Wroclaw 2, PO Box 937, Poland*

Abstract

Crystals of some ternary Chevrel-type compounds based on rare-earth molybdenum selenides ($REMo_6Se_8$) have been grown for RE = La, Ce, Pr, Nd and Sm. Refinement of the crystallographic data has confirmed the structure type expected for large ions, that is, the occupancy of the origin site of the rhombohedral-hexagonal lattice ($R\bar{3}$ symmetry). However, a systematic deficiency of the rare-earth content is observed (~84-94% of the total occupancy), leading to small changes of the physical properties (e.g. superconducting temperature T_c) as a function of concentration. Detailed analysis of the structural data is presented, both as a function of the cation content and its ionic radius. Lattice constant and interatomic distances are discussed in terms of electronic and steric effects. Superconducting properties are presented for several compounds since this is the first report on single crystal data obtained for rare-earth Chevrel-type selenides. Finally, a full comparison with the corresponding rare-earth molybdenum sulfides $REMo_6S_8$ is made. © 1997 Elsevier Science S.A.

Keywords: Chevrel phases; Magnetic superconductors; Crystal growth; Crystal structure; Structural transition

---

1. Introduction

Magnetic superconductors are one of the most challenging problems in solid-state physics. True coexistence of both superconductivity and long-range magnetic interactions only became possible when two fairly-independent crystallographic networks were fashioned in a three-dimensionnal lattice. Classical examples of this phenomenon are two families of ternary compounds (i.e. the Chevrel phases $REMo_6X_8$, X = S and Se, and the rhodium borides $RERh_4B_4$, both containing a rare-earth (RE) sublattice [1-3]). However, in order to distinguish and clearly separate both competing phenomena, single crystal measurements are absolutely necessary, since secondary phases may sometimes mask the essential properties of the desired compound.

In the case of Chevrel-type compounds containing rare-earth elements, the crystal growth was delayed for a long time, mainly because of the peritectic character of their melting. In the mid 1980s, we developed a suitable and successful method of growing single crystals of the sulfide series $REMo_6S_8$ leading to a thorough investigation of their physical and structural properties [4,5]. The selenide series $REMo_6Se_8$ was, however, more difficult to grow, in particular due to the existence of a stable secondary phase Mo_3Se_4 (Mo_6Se_8) of similar structural symmetry and of analogous superconducting properties.

In this work we present the first results obtained in single crystals of the selenide series, giving a short description of their growth method. Structural behaviour is discussed in terms of the rare-earth content and their atomic size, especially in the case of light rare-earths (La → Sm). Physical data are shown for a few cases, just to outline their general behaviour and to show some similarities when compared to the series of well-defined sulfides.

---

[*] Corresponding author. Tel.: +33 2 99286761; fax: +33 2 99635704; e-mail: pena@univ-rennes1.fr

0925-8388/97/$17.00 © 1997 Elsevier Science S.A. All rights reserved
PII S0925-8388(97)00344-7

2. Synthesis and crystal growth

Solid-state synthesis was carried out at 1200°C, mainly to describe the ternary diagram RE–Mo–Se. The specific example of RE = La allowed us to thoroughly define the homogeneity domain of the ternary Chevrel phase $LaMo_6Se_8$, but also to discover a new domain that occurs when minute amounts of La are inserted into the crystal structure of the binary matrix Mo_3Se_4 [6]. A striking property of the latter is the possibility of inserting all other rare-earth elements without destroying superconductivity. Furthermore, in the case of cations of ionic radius larger than 1 Å, the superconducting temperature T_c undergoes a systematic increase, no matter what the magnetic character of the dopant is [7,8].

Crystal growth was performed at high temperatures (~1700°C), starting essentially from mixtures composed of the appropriate ternary phase and the corresponding binary rare-earth selenide. Pellets of given overall composition were sealed under argon atmosphere inside a molybdenum crucible, then melted and subjected to slow cooling. Crystals containing light rare-earth elements (from La through Eu) all showed a single phase compound. In the case of heavy rare-earth elements, the method was found to be unsatisfactory due to a co-crystallization of the ternary phase and the binary Mo_3Se_4, as described earlier [9]. Details of the crystal growth parameters can be found in references [10,11].

3. Structural analysis

All $REMo_6Se_8$ crystals (RE = La, Ce, Pr, Nd and Sm) showed the expected Chevrel-phase crystal structure, composed of Mo_6Se_8 clusters and a pseudo-cubic site occupied by the rare-earth atom, stacked along the three-fold axis of the rhombohedral unit cell [12]. Two of the most important interatomic distances, i.e. the Mo–Mo intracluster distances are shown in Fig. 1, as a function of the lanthanum content. The observed behaviour is readily interpreted in terms of transfer of the electronic charge since, with increasing lanthanum content (from 0.84 up to 0.94 in Fig. 1), the corresponding VEC number increases from 22.52 up to 22.82 valence electrons per cluster (VEC) [10]. The increase in the total electronic charge in the cluster induces its contraction, as noticed by a decrease in the $(Mo_\Delta–Mo_\Delta)$ distance and a rather constant behaviour of the $(Mo–Mo)_\Delta$ distance (see caption of Fig. 1 for a full explanation of these distances).

Fig. 2 shows the same parameters, this time as a function of the ionic radius, for four particular systems (RE = La, Ce, Nd and Sm) having an average rare-earth content of 87%, i.e. for similar VEC numbers (the case of $Ce_xMo_6Se_8$ differs slightly since two crystals, having their respective cerium content at $x = 0.82$ and 0.92, were necessary to average out at the same $x = 0.87$ concentration). In this way, steric effects or the chemical pressure induced by big ions can give the same result on the interatomic distances as the electronic effects shown in Fig. 1.

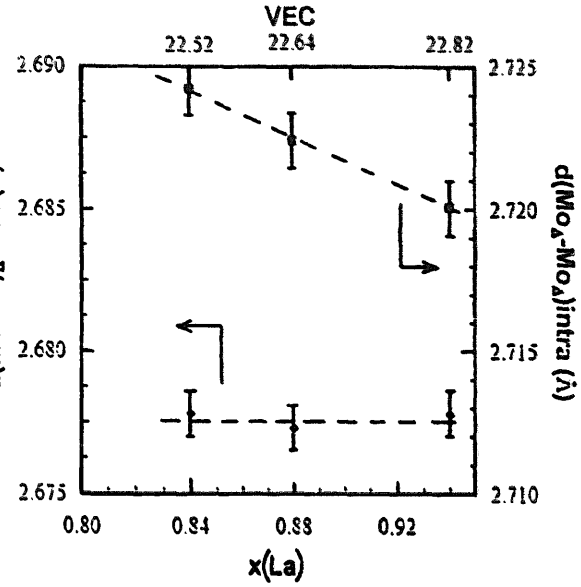

Fig. 1. Molybdenum–molybdenum intracluster distances as a function of the lanthanum (bottom) and the VEC (top) concentrations, for three single crystals of the $La_xMo_6Se_8$ phase. The distances are defined as $d(Mo–Mo)_\Delta$ and $d(Mo_\Delta–Mo_\Delta)$ for molybdenum atoms situated in the same plane and on neighbouring planes, respectively, perpendicular to the ternary axis.

It should be noted at this point that, whatever our different trials of crystal growth by varying the temperature conditions or the starting composition of the melt, a systematic deficiency of the rare-earth content

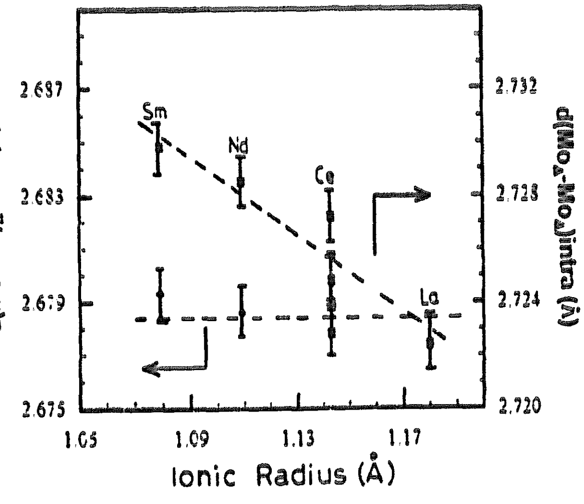

Fig. 2. Molybdenum–molybdenum intracluster distances (defined in Fig. 1) as a function of the ionic radius for single crystals of $RE_xMo_6Se_8$ (RE = La, Ce, Nd and Sm), all of them having approximately the same concentration $x \sim 0.87$ (see text).

was observed, always situated between $x = 0.84$ and 0.95, i.e. inside the domain of homogeneity of the Chevrel phase. This may be a characteristic feature of the selenide series, not observed in their sulfide counterparts [5]; it may be related to the overall VEC number of the Mo_6X_8 cluster, thus resulting in an inclination of the Chevrel phase domain at high temperatures (at the level of 1700°C or above) towards the Mo–Se binary line.

4. Physical properties

A thorough determination of the magnetic and superconducting properties measured in single crystals of the above-mentioned compounds was made by standard dc and ac techniques [10]. Transport properties were also investigated by resistivity methods. For comparison, the same measurements were performed in the binary compound Mo_3Se_4 (Mo_6Se_8). In this latter case, a critical field $Hc_2(0)$ of approximately 8 T was obtained with a weak magnetic anisotropy of approximately 12%; all this in agreement with previous measurements performed in polycrystalline samples [13].

Particularly interesting is the ternary compound $LaMo_6Se_8$ having an extraordinarily high critical field $Hc_2(0)$ of 55 T when extrapolated to zero temperature. This value, already announced in powder specimens [14,15], is comparable to the one obtained in the well-known $PbMo_6S_8$ compound and confirms all expectations for these materials for technological applications.

Novel results were obtained in the case of RE = Ce and Eu, i.e. two non-superconducting $REMo_6Se_8$ compounds which showed resistance anomalies at 9 and 95 K, respectively. The first one corresponds to the onset of a Kondo behaviour, similar to the one observed in the sulfide counterpart [16], and it is followed by a sharp decrease of its resistance at 2 K. In the case of $Eu_xMo_6Se_8$, two different behaviours of ρ(T) were observed between room-temperature and the structural transition T_s (~95 K) [17]: (i) metallic behaviour with a linear decrease of resistance; and (ii) semi-metal-like increase of $\rho(T)$ down to T_s (Fig. 3). These two behaviours have been related to two kinds of occupation at the origin site of the structure by the europium atoms, one of which may be slightly shifted along the ternary axis [17].

$NdMo_6Se_8$ and $PrMo_6Se_8$ superconduct at 8.35 K and 9.05 K, respectively, the former presenting a strong magnetic anisotropy, as evidenced by crystal field effects at low temperatures. Their resistance behaviour show (Fig. 4), as in all single crystals of this series, a marked saturation of resistance at high temperatures which may occur when the mean free path of the electrons becomes of the order of the lattice spacing [18]. It should be also noted that, contrary to the sulfide series [5], all crystals reported in this paper showed a high absolute value of resistance at room-temperature (typically 1 or 2 mΩ cm) and very low resistivity ratios RRR (of the order of 1 or 2). This behaviour can be explained by the larger interatomic distances in the selenides series compared to sulfides and by the extreme brittleness of crystals due to weaker Mo–Se bonding compared to the Mo–S bonding.

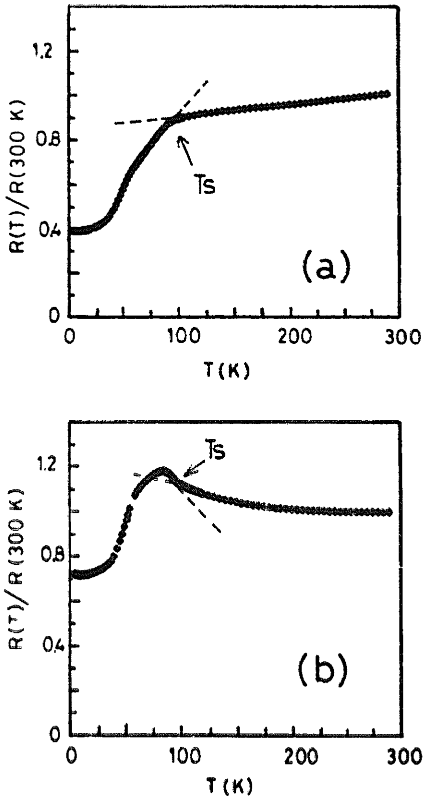

Fig. 3. Resistivity (normalized to room temperature values) of two single crystals of $EuMo_6Se_8$. Respective compositions, as determined from structural refinement are: (a) $Eu_{0.896}$ $Eu_{0.084}Mo_6Se_{7.92}$; (b) $Eu_{0.98}Mo_6Se_8$ (T_s gives an estimate of the structural transition temperature).

For completeness, we show typical magnetic behaviour observed in $Ho_xMo_6Se_8$ crystals (Fig. 5): a

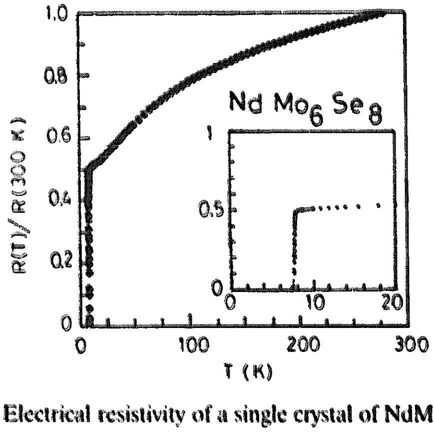

Fig. 4. Electrical resistivity of a single crystal of $NdMo_6Se_8$.

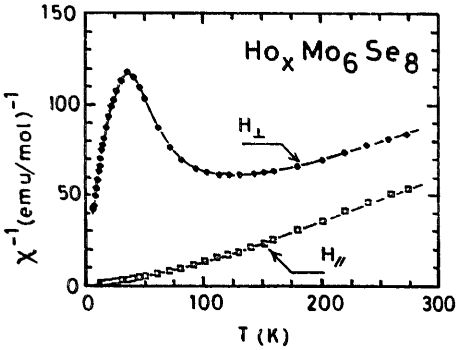

Fig. 5. Inverse magnetic susceptibility measured under a 0.1 T field for an ensemble of crystals of $Ho_xMo_6Se_8$. The applied field was applied parallel and perpendicular to the [111] ternary axis (by analogy to $HoMo_6S_8$ of Burlet et al. [19]).

very strong magnetic anisotropy (Ising type, as in the case of the ferromagnetic superconductor $HoMo_6S_8$ [19]) is present at low temperature, with an easy direction of magnetization along the ternary [111] axis. No re-entrant superconductivity was observed but, as pointed out above, our specimens based on heavy rare-earth elements are always bi-phased, composed of the ternary magnetic phase and the non-magnetic binary Mo_3Se_4 phase. As a result, a very low percentage of holmium (roughly evaluated to 25–35%) is present in the crystal: this precludes the onset of magnetic interactions inside the superconducting state. More work is still necessary in order to grow single crystals of this very interesting phase, free of Mo_3Se_4 intergrowths.

In conclusion, this work has shown the first results obtained on single crystals of several rare-earth molybdenum selenides $REMo_6Se_8$. A thorough understanding of their structural behaviour, both as a function of the rare-earth content and the ionic size, was obtained, at least for the members from RE = La up to Sm. The europium case is particularly interesting since slight modifications of the crystal structure may change the electronic properties drastically. In all cases, the intrinsic basic (magnetic and transport) properties have been investigated and reported. The case of the heavy rare-earth representatives, the most interesting because of the co-existence of superconductivity and magnetism, has unfortunately not been solved yet, and more work is still necessary in this field.

References

[1] Ø. Fischer, A. Treyvaud, R. Chevrel, M. Sergent, Solid. State. Comm. 17 (1975) 721.
[2] R.N. Shelton, R.W. Mc Callum, H. Adrian, Phys. Lett 56A (1976) 213.
[3] B.T. Matthias, E. Corenzwit, J.M. Vandenberg, H. Barz, Proc. Natl. Acad. Sci. USA 74 (1977) 1334.
[4] R. Horyń, O. Peña, C. Geantet, M. Sergent, Supercond. Sci. Technol. 2 (1989) 71.
[5] O. Peña, M. Sergent, Prog. Solid State Chem. 19 (1989) 165.
[6] R. Horyń, F. Le Berre, A. Wojakowski, O. Peña, Supercond. Sci. Technol. 9 (1996) 1081.
[7] F. Le Berre, D. Tshimanga, A.-L. Guilloux, J. Leclercq, M. Sergent, O. Peña, R. Horyń, A. Wojakowski, Physica. B 228 (1996) 261.
[8] F. Le Berre, O. Peña, C. Hamard, A. Corrignan, R. Horyń, A. Wojakowski, this conference.
[9] R. Horyń, O. Peña, A. Wojakowski, M. Sergent, Supercond. Sci. Technol. 7 (1994) 146.
[10] F. Le Berre, Thesis, Université de Rennes I (France) (1996).
[11] F. Le Berre, O. Peña, C. Perrin, M. Sergent, R. Horyń, A. Wojakowski, submitted.
[12] R. Chevrel, M. Sergent, Topics in Current Physics,vol. 32; Ø. Fischer, M.B. Maple (Eds.) Springer-Verlag (1982), pp. 25–86.
[13] M. Decroux, Ø. Fischer, Topics in Current Physics, vol. 34; M.B. Maple, Ø. Fischer (Eds.) Springer-Verlag (1982), pp. 57–98.
[14] S. Foner, E.J. Mc Niff, Jr., R.N. Shelton, R.W. Mc Callum, M.B. Maple, Phys. Lett. 57A (1976) 345.
[15] Ø. Fischer, M. Decroux, M. Sergent, R. Chevrel, J. Phys. Coll. (France) 39 (1978) C2–257.
[16] O. Peña, C. Geantet, R. Horyń, M. Potel, J. Padiou, M. Sergent, Mat. Res. Bull. 22 (1987) 109.
[17] F. Le Berre et al., to be published.
[18] Z. Fisk, G.W. Webb, Phys. Rev. Lett. 36 (1976) 1084.
[19] P. Burlet, A. Dinia, S. Quézel, W.A.C. Erkelens, J. Rossat-Mignod, R. Horyń, O. Peña, C. Geantet, M. Sergent, J.L. Genicon, Physica. B. 148 (1987) 99.