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New superconducting materials based upon doping of the Chevrel-phase binary compound Mo_6Se_8

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Abstract

Superconducting properties of the binary phase Mo_6Se_8 have been enhanced by the insertion of minute amounts of large-sized ions. These ions occupy one of the void sites of the Chevrel-phase structural skeleton, that is, at the origin of the rhombohedral–hexagonal lattice ($R\bar{3}$ symmetry) but a maximum of 10% only of these sites can be filled. Physical properties (e.g. electrical resistivity, magnetic behaviour, etc.) of these doped materials are very similar to those of the undoped compound. However, an important increase of the superconducting temperature (from 6.45 K, for the pure Mo_6Se_8 binary, up to a maximum of 7.1 K for the most doped samples) is systematically observed, no matter the magnetic character or the oxidation state of the ion. The only important parameter seems to be the ionic radius of the dopant, which in turn may modify the position of the Fermi level on the density of states. Particularly interesting is the case of rare-earth ions such as trivalent Ce and divalent Eu which, among others, produce some of the largest increases of T_c; these same rare-earths are known to suppress superconductivity of the ternary Chevrel phases $REMo_6Se_8$. Small-sized ions (heavy rare-earths, U, Cu or Ag, for instance) have no influence on the superconducting temperature of the starting compound. © 1997 Elsevier Science S.A.

Keywords: Chevrel phases; Magnetic superconductors; Structural transition; New materials; Doped materials

1. Introduction

Among the Chevrel-phase compounds ($M_x^{n+}Mo_6X_8$, X = S, Se, Te) those containing rare-earth ions (M = RE) are particularly interesting because of coexistence phenomena between superconductivity and magnetic order [1,2]. It should be emphasized, however, that the cerium-based compound is not superconducting neither in the sulfide series nor in the selenide one. The europium compound $EuMo_6S_8$ superconducts only under 10 kbar while the selenide counterpart $EuMo_6Se_8$ stays metallic, even under high external pressures [3,4]. Alkaline-earth derivatives (i.e. when M = Ca, Sr, Ba) present similar behaviours as those of europium, that is, a structural transition from a high-temperature rhombohedral phase towards a low-temperature non-superconducting triclinic phase [4,5]. Here again, the application of external or chemical (due to vacancies) pressures may inhibit the structural transition and the compounds turn into a superconducting material [6–8].

A particular case among these superconductors concerns the binary compound itself Mo_6Se_8 [9]. Its structure is based on the same skeleton as the Chevrel ternaries, that is, stacking of Mo_6Se_8 clusters along the ternary axis of the rhombohedral symmetry, together with a pseudo-cubic site at the origin of the unit cell. This site is filled up to 100% in the ternaries while it stays empty in the binary phase. However, as

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we reported in references [10,11], it is possible to dope the binary compound by partially filling the site at the origin of the unit cell with very small amounts of lanthanum, preserving the structural and physical properties of the matrix. In the course of these investigations, we found a quite important increase of T_c (from 6.45 K in the void compound up to 7.1 K in the 'doped' material). We have extended this research to all lanthanide and alkaline-earth ions, together with other big (e.g. Pb, Sn,...) or small (e.g. Cu, U, Ag,...) ions. In this work, we present our latest results on this system, pointing out the eventual differences between these several cases and making a full comparison with the ternary Chevrel-phase materials cited above.

2. Synthesis and results

Solid-state synthesis was performed at 1200°C using metallic molybdenum (previously reduced under hydrogen flow at 900°C) and binary selenides ($MoSe_2$ and MSe_y), these latter prepared by solid-gas reaction of selenium vapors onto the hot metal. The exact selenium content y(Se) of the starting binary was calculated from the weight loss after oxidation of small amounts of the selenide material.

Nominal composition of all samples was chosen close to the Mo_6Se_8 formula, that is $\underline{(Mo_6Se_8)}M_x$, where the maximum content x(M) was always kept below 0.7 at. % M per Mo_6Se_8 cluster. This choice comes from the fact that at higher ion concentration (of the order of 1–1.5 at. % M and above), samples become multi-phased, containing both the doped binary phase and the Chevrel ternary phase [10]. With such small content x(M), special care should be taken during sample preparation, since required quantities of the selenide MSe_y would be of the order of 10 mg. In some cases, a dilution technique was used, that is, mixing appropriate amounts of an already synthesized $M_1Mo_6Se_8$ ternary phase with a pure Mo_6Se_8 binary phase. Final results (i.e. lattice parameters and T_c) are independent of the method used. In either case, estimation of error in the x content is of the order of 0.02 at. % M.

X-ray powder diffraction patterns of the resulting materials were indexed similarly to the well-known $R\bar{3}$ symmetry of Mo_6Se_8 [9]. The crystal structure was also resolved by analogy to the Mo_6Se_8 structure in a $R\bar{3}$ space group [12], confirming the partial occupation of the origin site by the dopant, although a slight shift (approx. 1 Å) of its position along the ternary axis may be observed (full results on X-ray single crystal structural refinement will be reported in a separate work [13]).

Table 1 gives the superconducting critical temperature T_c of all materials tested in this work. All samples have been found superconducting, including those containing cerium, europium and alkaline-earth ions (which are not superconductors in the case of the Chevrel ternary phases). Absolutely no degradation of T_c with respect to that of the matrix (Mo_6Se_8, T_c = 6.45 K) was observed, keeping a full 100% Meissner effect as determined from a.c. susceptibility measurements. In some cases, resistivity was measured in single crystal specimens, showing a very sharp transition at T_c [11]. Magnetization measurements performed in a SQUID susceptometer confirmed a bulk superconductivity and provided the oxidation state of some specific cations. For instance, it was shown that cerium and ytterbium were in trivalent states while europium was in a magnetic divalent state [11].

Figs. 1 and 2 show some examples of superconducting transitions for M = Gd, Eu, Tb, Pr and Pb, while Figs. 3 and 4 show the T_c dependence on the cation concentration, in the cases of rare-earth (M = Eu, Ce, Gd and Y) and alkaline-earth (M = Ca, Sr and Ba) materials.

Table 1

Critical temperatures T_c(K) of $\underline{(Mo_6Se_8)}M_x$ (x in units of atomic percentage; T_c values given at ± 0.05 K, x values given at ± 0.02 at. %)

x (% at.)	Y	U	Ag	Cu	Sn	In	Pb	Ca	Sr	Ba
0.21 (2)										7.10
0.35 (2)	6.46	6.42	6.42	6.55	6.76	6.79	7.10	6.80	6.95	
0.43 (2)										7.10
0.70 (2)	6.43	6.42	6.50	6.55	6.85	6.74	7.10	7.00	7.08	7.10

x (% at.)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb
0.35 (2)	6.80	6.70	6.62	6.62	6.55	6.90	6.44	6.42	6.46	6.43	6.43	6.43
0.70 (2)	7.05	6.81	6.89	6.71	6.70	7.10	6.47	6.45	6.46	6.45	6.46	6.46

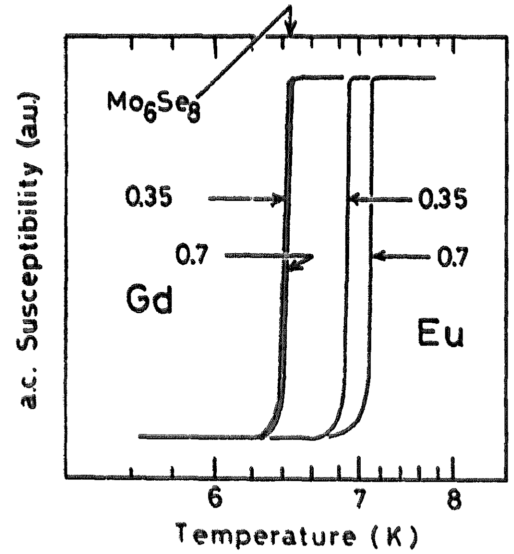

Fig. 1. Inductive transitions of $\underline{(Mo_6Se_8)}RE_x$, for RE = Eu and Gd and for x = 0.35 and 0.7 at. % RE (vertical arrow shows the critical temperature of the undoped binary).

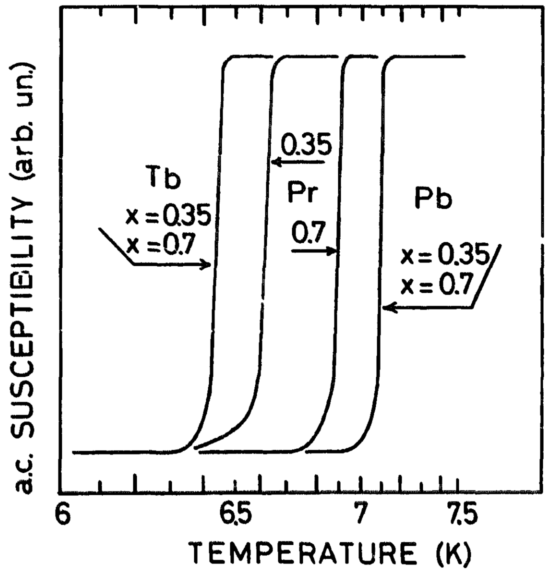

Fig. 2. Inductive transitions of $(Mo_6Se_8)M_x$, for M = Tb, Pr and Pb and for $x = 0.35$ and 0.7 at. % M.

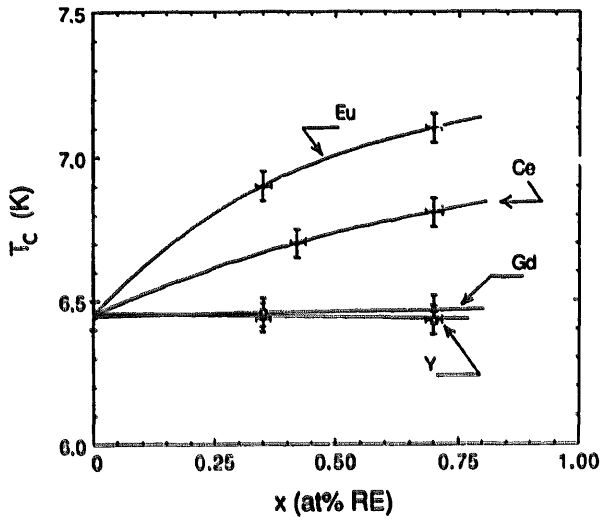

Fig. 3. Critical temperature of $(Mo_6Se_8)RE_x$, for RE = Eu, Ce, Gd and Y as a function of concentration.

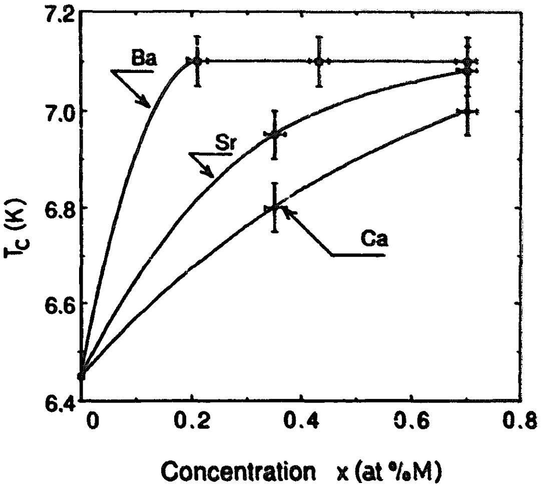

Fig. 4. Critical temperature of $(Mo_6Se_8)M_x$, containing the alkaline-earth elements (Ca, Sr and Ba) as a function of concentration.

3. Discussion

It is quite obvious from Fig. 1 that magnetism has no effect on the superconducting state. For instance, Gd^{3+} and Eu^{2+} ions, both having the same electronic configuration, influence the superconducting transition in a quite different manner: the former does not change the critical temperature, T_c, of the Mo_6Se_8 matrix, while the latter makes T_c to increase towards a maximum value of approx. 7.1 K. It is also evident from Fig. 3 that cerium ion does not suppress T_c, although it is well known the admixture between the cerium 4f-level and the conduction band which leads to catastrophic effects on superconductivity (e.g. in $CeMo_6X_8$). Also, equivalent rare-earth ions such as Y and La, containing no 4f electrons, have different effects on T_c, the former showing no influence on the critical temperature of the matrix (Fig. 3) while the latter shows one of the largest increases ever obtained.

Charge transfer from the ion towards the Mo_6 cluster has no direct influence either, on the superconducting behaviour, as evidenced by the similar values of T_c for divalent dopants (Eu^{2+}, Ca^{2+}, Sr^{2+}, etc) or trivalent ones (La^{3+}, Ce^{3+}). Also, if one compares, for instance, the light rare-earth ions (La, Ce, Pr, Nd, Sm) to the heavy ones (Gd, Tb, Dy, Ho, Er,...), all in a trivalent state, it is quite obvious that their T_c dependences behave quite differently.

It is also good to point out the strikingly similar values obtained for the Mo_6Se_8 matrix doped with Eu^{2+} and Sr^{2+} of same concentrations (Table 1). Note that both ions have the same radius. Fig. 4 shows, in particular, that the superconducting critical temperature saturates towards a fixed value (approx. 7.1 K) much quicker when the ion has a larger ionic radius, situation also found for Pb. Contrary to that, when the dopant is of smaller size (e.g. Ce, Pr or Ca), T_c increases at a lower rate. It should be stressed at this point that it is not possible to increase the amount of dopant above ~ 0.7 at. % (for instance, in order to reach saturation of T_c) without turning into a biphased region composed of the above-mentioned doped binary and the corresponding Chevrel ternary phase [10].

All these results have then been plotted in Figs. 5a,b as a function of the ionic radius, the latter evaluated in reference [14] for a coordination number of eight in most of the cases. A clear threshold value at $r \sim 1.05$ Å is found, which separates a region of constant T_c from a region where T_c is rapidly increasing with the ionic radius. It is possible that a pressure effect on the cluster due to the big ions, may be the

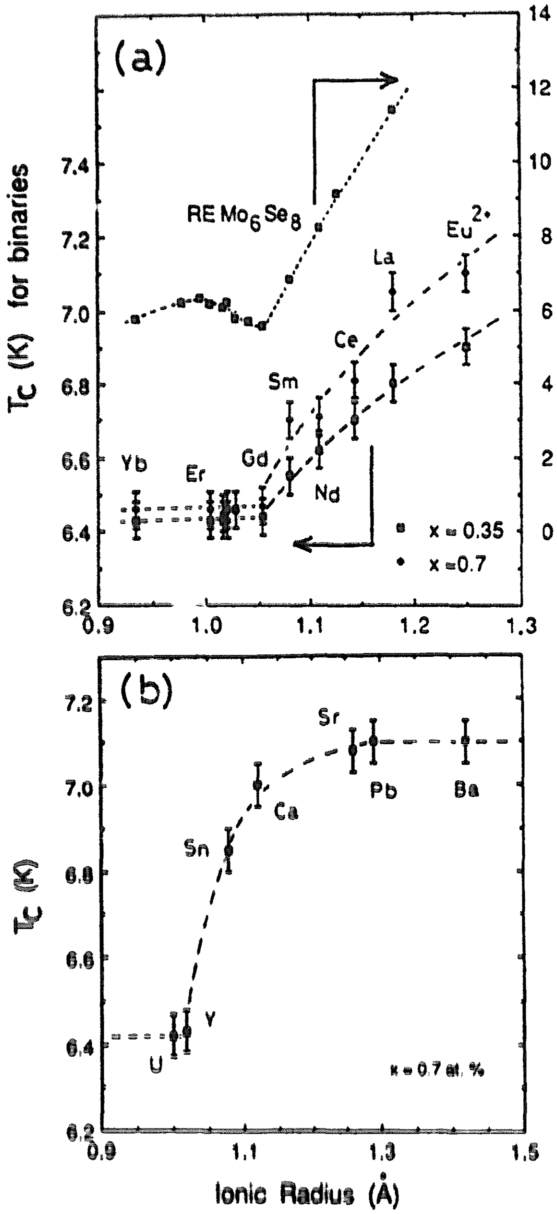

Fig. 5. Critical temperature of $(Mo_6Se_8)M_x$ as a function of the ionic radius of the M elements: (a) case of the rare-earth ions; (b) case of alkaline-earth elements and other big ions [for comparison, the T_c variation for the Chevrel ternary phases $REMo_6Se_8$ is also shown in (a)].

reason for such important T_c dependence; however, it has been shown that application of external pressure on polycrystalline Mo_6Se_8 made T_c being depressed by an important factor [15].

In our opinion, a subtle modification in the density of states of these materials occurs because of the cell-volume expansion, which may produce an important shift in the position of the Fermi level thus inducing a big change of T_c. It is good to recall that a similar variation of T_c is observed in the $REMo_6Se_8$ series (Fig. 5a), but no clear explanation has been given up to now on this phenomenon. The striking similarity in the T_c variation for both series presented herein (the ternary phases and doped binaries) impose a unique model, which should take into account the steric effects due to the insertion of big-sized ions.

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