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Synthesis and Electrical Properties of New Chalcogenide Compounds Containing Mixed (Mo, *Me*)$_6$ Octahedral Clusters (*Me* = Ru or Rh)

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We report the synthesis and some properties of new compounds and some solid solutions containing mixed octahedral $(Me)_6$ clusters (Me = Mo, Ru, Rh). The compound $Mo_4Ru_2Se_8$ is semiconducting whereas the limit compounds $Mo_4Ru_2Te_8$ and $Mo_{4.66}Rh_{1.33}Te_8$ are metallic. Superconductivity was found around the composition Mo_5RuTe_8.

Introduction

The compounds of the type $M_xMo_6X_8$ (*1*) (M = metal, X = S, Se, Te) are well known for their exceptional superconducting properties (*2*). These properties are closely related to the presence of octahedral Mo_6 clusters in these materials. It is therefore of particular interest to substitute Mo wholly or partly by other transition metals. Following these ideas, we earlier reported the synthesis and properties of $Mo_2Re_4S_8$, $Mo_2Re_4Se_8$, and $Mo_4Re_2Te_8$ which have mixed Me_6 clusters (Me = Mo, Re) (*3*). In the present work, we present new compounds having mixed Mo–Ru and Mo–Rh clusters: $Mo_4Ru_2Se_8$, $Mo_4Ru_2Te_8$, $Mo_{4.66}Rh_{1.33}Te_8$, and some solid solutions.

Sample Preparation

The compounds were prepared by direct synthesis in sealed evacuated quartz ampoules at 1150°C. Starting materials were purissimum grade Fluka chalcogenides and pure (≥99.9%) powdered metals (Climax Molybdenum Corp. for Mo, Ventron for Ru, and Fluka for Rh). For the measurements of T_c and resistivity, the powders were pressed into pellets and sintered at 1150°C.

The Pseudobinary Compounds

Three new compounds were found: $Mo_4Ru_2Se_8$, $Mo_4Ru_2Te_8$, and $Mo_{4.66}Rh_{1.33}Te_8$. Pure compounds were obtained for the above compositions; slightly different compositions lead to production of impurities, mainly MoX_2, RuX_2, and Ru or Rh, so no nonstoichiometry was detected for these pseudobinary compounds. We did not succeed in preparing the corresponding sulfides and the selenide in the case of Rh, under the above conditions.

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The three compounds crystallize in a hexagonal–rhombohedral lattice with space group $R\bar{3}$ as the compounds Mo_6X_8 (*5*) and $M_xMo_6X_8$ ($X = S, Se, Te$) (*1, 4*). The unit-cell volume of these new compounds is lower than that of the Mo_6X_8 binary compound, excluding the possibility of Ru and Rh being inserted in the structure outside of the Mo_6 cluster as in $M_xMo_6X_8$ compounds. The main difference between the lattice parameters of the two binaries Mo_6X_8 (X = Se, Te) and the three new compounds is that the rhombohedral angle increases significantly in the latter (Table I). This was also the case for the $Mo_2Re_4X_8$ compounds and for the pseudobinaries $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ (*6*). A similar situation was earlier observed in $Cu_xMo_6S_8$ where the rhombohedral angle increases as the Cu concentration is increased (*1, 7*). The common feature of all these pseudobinaries and the $Cu_xMo_6S_8$ compounds is that the number of electrons on the Me_6 cluster is increased with respect to the binaries and so it appears that the increase in α_{Rh} is directly correlated with this increase in the number of electrons on the cluster.

The physical properties of these pseudobinaries are also closely related to the number of electrons on the Me_6 cluster. In $Mo_4Ru_2Se_8$, $Mo_4Ru_2Te_8$, as well as the earlier-reported $Mo_2Re_4S_8$, and $Mo_2Re_4Se_8$, the Me_6 cluster has 24 electrons (we assume here the chalcogens to have the valency (−2)). Band calculations (*8, 9*) for the $M_xMo_6S_8$ compounds show that there should be a band gap at 24 electrons and, in fact, $Mo_4Ru_2Se_8$, $Mo_2Re_4S_8$, and $Mo_2Re_4Se_8$ are

TABLE I

LATTICE PARAMETERS FOR PSEUDOBINARY COMPOUNDS OF THE TYPE $Mo_{6-x}M_xX_8$ (M = Nb, Re, Ru, Rh, Ta) (X = S, Se, Te) and $Mo_6X_{8-y}Y_y$ (Y = Cl, Br, I)

Compounds (Ref.)	T_c (K)	Hexagonal parameters (Å)		Rhombohedral parameters (Å)	(°)	V_H (Å^3)
Mo_6S_8 (*5*)		$a = 9.20$	$c = 10.88$	$a = 6.43$	$\alpha = 91°96$	797
$Mo_2Re_4S_8$ (*3*)	Semicon.	$a = 9.34$	$c = 10.42$	$a = 6.41$	$\alpha = 93°43$	787
$Mo_6S_6Br_2$ (*6*)	13.8	$a = 9.54$	$c = 10.36$	$a = 6.50$	$\alpha = 94°43$	817
$Mo_6S_6I_2$ (*6*)	14.0	$a = 9.64$	$c = 10.44$	$a = 6.56$	$\alpha = 94°50$	841
Mo_6Se_8	6.25	$a = 9.57$	$c = 11.15$	$a = 6.66$	$\alpha = 91°85$	884
$Mo_2Re_4Se_8$ (*3*)	Semicon.	$a = 9.67$	$c = 10.74$	$a = 6.63$	$\alpha = 93°61$	870
$Mo_4Ru_2Se_8$	Semicon.	$a = 9.69$	$c = 10.82$	$a = 6.65$	$\alpha = 93°41$	879
$Mo_6Se_5Cl_3$[a]	5.7	$a = 9.64$	$c = 11.05$	$a = 6.67$	$\alpha = 92°40$	889
$Mo_6Se_5Br_3$ (*10*)	7.1	$a = 9.82$	$c = 10.83$	$a = 6.72$	$\alpha = 93°86$	904
$Mo_6Se_5I_3$ (*10*)	4.2	$a = 10.02$	$c = 10.73$	$a = 6.80$	$\alpha = 94°89$	933
$Mo_{5.25}Nb_{0.75}Se_8$[b]	6.2	$a = 9.60$	$c = 11.16$	$a = 6.68$	$\alpha = 91°96$	892
Mo_6Te_8 (*5*)	<1.7	$a = 10.20$	$c = 11.66$	$a = 7.04$	$\alpha = 92°60$	1050
$Mo_4Re_2Te_8$ (*3*)	3.5	$a = 10.22$	$c = 11.51$	$a = 7.04$	$\alpha = 93°08$	1041
$Mo_4Ru_2Te_8$	<1.7	$a = 10.28$	$c = 11.35$	$a = 7.03$	$\alpha = 93°82$	1037
$Mo_6Te_6Cl_2$[a]		$a = 10.19$	$c = 11.68$	$a = 7.05$	$\alpha = 92°47$	1050
$Mo_6Te_5Br_3$ (*10*)		$a = 10.20$	$c = 11.66$	$a = 7.04$	$\alpha = 92°60$	1050
$Mo_6Te_5I_3$ (*10*)	2.4	$a = 10.32$	$c = 11.51$	$a = 7.09$	$\alpha = 93°46$	1061
$Mo_{5.25}Nb_{0.75}Te_8$[b]	<1.7	$a = 10.21$	$c = 11.70$	$a = 7.07$	$\alpha = 92°49$	1057
$Mo_{5.25}Ta_{0.75}Te_8$[b]	<1.7	$a = 10.21$	$c = 11.70$	$a = 7.07$	$\alpha = 92°48$	1056
$Mo_{4.66}Rh_{1.33}Te_8$	<1.7	$a = 10.25$	$c = 11.53$	$a = 7.06$	$\alpha = 93°15$	1049

[a] C. Perrin, private communication.

[b] A. Perrin, unpublished results.

semiconducting. The tellurides $Mo_4Ru_2Te_8$ and $Mo_{4.66}Rh_{1.33}Te_8$ are, on the contrary, metallic. This is not very surprising since already in the $Mo_2Re_4X_8$ compounds it was found that the energy is reduced as one goes from the sulfide to the selenide, and it extrapolated to zero at a composition intermediate between $Mo_2Re_4Se_8$ and "$Mo_2Re_4Te_8$" (however, the latter compound does not form). Thus, the results found with the Ru and Rh compounds are consistent with the earlier results with the Re compounds. The reason that the Te compound is metallic is, we believe, that the Te 5*p* levels admix more with the 4*d* levels than the 4*p* or 3*p* levels in the selenides and the sulfides, respectively, so that the gap closes and the Te no longer can be considered as exactly divalent.

Contrary to the compounds with 24 cluster electrons, the compounds with ≈22 cluster electrons are metallic and generally superconducting. Examples published earlier are $Mo_6S_6Br_2$, $Mo_6S_6I_2$, and $Mo_4Re_2Te_8$. In this investigation, we found that Mo_5RuTe_8 is superconducting at ~2.0 K.

Solid Solutions

1. $Mo_4Ru_2Se_8$–Mo_6Se_8

Figure 1 shows the variation of the lattice parameters in the series $Mo_{6-x}Ru_xSe_8$. A homogeneity domain extends from $x = 0$ to $x = 1.25$, and a second, very narrow, domain is centered around $x = 2$, leaving an inhomogeneous domain between $x = 1.25$ and $x = 2$. We note that, if we extrapolate the lattice parameters from the $x < 1.25$ region to $x = 2$, we get nearly the lattice parameters of $Mo_4Ru_2Se_8$; thus the appearance of the inhomogeneous region is not followed by a break in the lattice parameters. The only clear difference between $Mo_4Ru_2Se_8$ and the compounds for $x < 1.25$ is that the latter are metallic whereas the former is semiconducting, and the appearance of the inhomogeneous region is probably closely connected to this change in electronic properties.

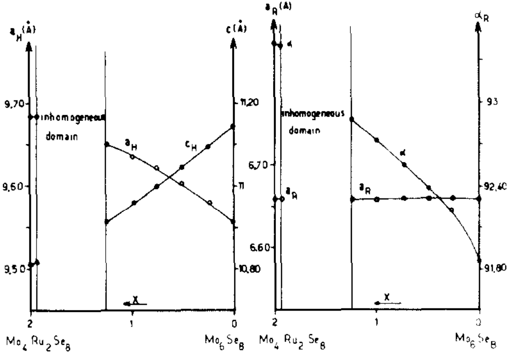

FIG. 1. Hexagonal and rhombohedral lattice parameters for the solid solution $Mo_{6-x}Ru_xSe_8$.

Note also that the rhombohedral lattice parameter a_R is practically constant whereas the rhombohedral angle α_R increases as we replace Mo by Ru. This is consistent with the assumption that α_R is correlated with the charge transfer.

In Fig. 2, we show the superconducting critical temperature, which decreases very quickly as x is increased.

2. $Mo_4Ru_2Te_8$–Mo_6Te_8

The lattice constants for the series $Mo_{6-x}Ru_xTe_8$ are shown in Fig. 3. In this

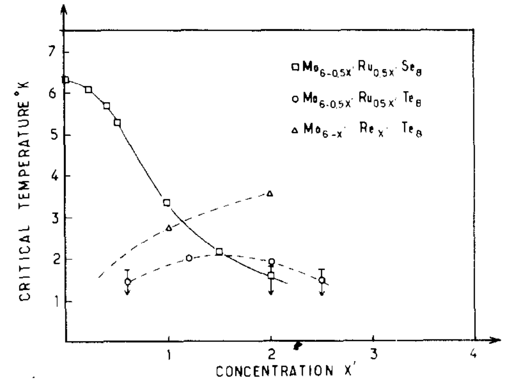

FIG. 2. Superconducting critical temperature for $Mo_{6-0.5x'}Ru_{0.5x'}Se_8$, $Mo_{6-0.5x'}Ru_{0.5x'}Te_8$, and $Mo_{6-x'}Re_{x'}Te_8$. x' represents the number of electrons added to the Me_6 cluster by the substitution of Re or Ru for Mo. Note the relation $x' = 2x$.

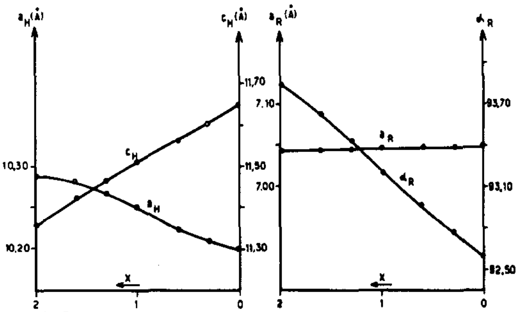

FIG. 3. Hexagonal and rhombohedral lattice parameters for the solid solution $Mo_{6-x}Ru_xTe_8$.

series, the solid solution exists throughout the domain $0 \leq x \leq 2$. This is consistent with the result found above, since here both $Mo_4Ru_2Te_8$ and Mo_6Te_8 are metallic. Note that, as x increases α_R increases, whereas a_R remains constant, exactly as we found above for $Mo_{6-x}Ru_xSe_8$.

Neither $Mo_4Ru_2Te_8$ nor Mo_6Te_8 were found to be superconducting. However, since $Mo_4Re_2Te_8$ having formally 22 cluster electrons was found earlier to be superconducting, it was of interest to look for superconductivity around Mo_5RuTe_8. In Fig. 2, T_c is also plotted for this series and one finds indeed that superconductivity appears around Mo_5RuTe_8, with a maximum T_c equal to 2.1 K for $Mo_{5.4}Ru_{0.6}Te_8$. For comparison, we also show T_c for two compositions in the $Mo_{6-x}Re_xTe_8$ series.

3. $Mo_4Ru_2Se_8$–$Mo_4Ru_2Te_8$

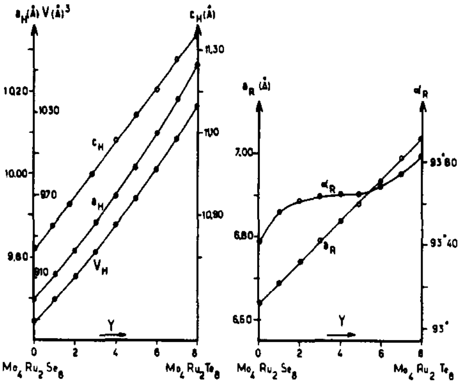

FIG. 4. Hexagonal and rhombohedral lattice parameters for the solid solution $Mo_4Ru_2Se_{8-y}Te_y$.

Since $Mo_4Ru_2Se_8$ is semiconducting and $Mo_4Ru_2Te_8$ is metallic, it seemed to us of particular interest to look for a solid solution $Mo_4Ru_2Se_{8-y}Te_y$. It turns out that this solid solution is possible in the whole domain $0 \leq y \leq 8$, and the lattice parameters shown in Fig. 4 do not reveal any anomalies which would indicate a transition from the semiconducting to the metallic phase. Resistance measurements show that this transition takes place between $y = 1.0$ and $y = 1.3$. In Fig. 5 is shown the resistance ratio $\rho(T)/\rho(300)$ as a function of temperature for different values of y. It is surprising that there is not an inhomogeneous domain between the semiconducting and the metallic regions. However, there is a difference between the $Mo_{6-x}Ru_xSe_8$ series considered above and this series since in the former the metal–

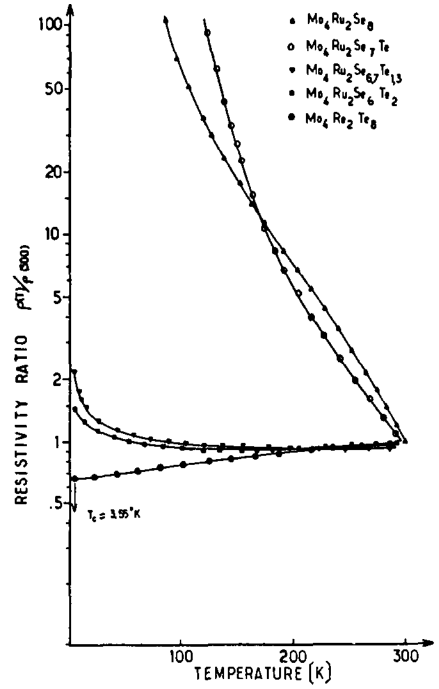

FIG. 5. Resistance ratio $\rho(T)/\rho(300)$ for $Mo_4Ru_2Se_{8-y}Te_y$ ($y = 0, 1, 1.3, 2$) and $Mo_4Re_2Te_8$.

semiconductor transition is reached by filling a band, wheras in $Mo_4Ru_2Se_{8-y}Te_y$, the transition is certainly a result of the gap disappearing. Since there is no anomaly in the lattice parameter between $y = 1$ and $y = 2$, we believe that the bands above and below the gap merge in a continuous fashion, so that the compounds with $y > 1.2$ are in fact semimetals. This is consistent with the low-temperature increase of the resistance, although we cannot exclude this as being due to fluctuations in concentration so that part of the sample is still semiconducting. For comparison, we also show in Fig. 5 the resistance ratio for the superconducting compound $Mo_4Re_2Te_8$ ($T_c = 3.55$ K).

Conclusion

The properties of the new compounds of the type $Mo_{6-x}M_xX_8$ (M = Re, Ru, Rh; X = S, Se, Te) are mainly determined by the number of electrons on the Me_6 cluster. This is consistent with the assumption that the *Me* *d*-electrons are responsible for the electrical conduction in these materials. In particular, the appearance of semiconductivity in $Mo_2Re_4S_8$, $Mo_2Re_4Se_8$, and $Mo_4Ru_2Se_8$ is in agreement with band calculations. The appearance of superconductivity in Mo_5RuTe_8 ($T_c \simeq 2$ K) was expected since $Mo_4Re_2Te_8$ is superconducting ($T_c \simeq 3.55$ K). On this basis, we also expect the composition near $Mo_{5.3}Rh_{0.7}Te_8$ to be superconducting, though somewhat lower than 1.7 K which was the lower limit in the present experiment.

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