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Stabilization of Mo_6S_8 by Halogens; New Superconducting Compounds: $Mo_6S_6Br_2$, $Mo_6S_6I_2$

MARCEL SERGENT[*], ØYSTEIN FISCHER, AND MICHEL DECROUX

Département de Physique de la Matière Condensée, Université de Genève 24, quai Ernest Ansermet, 1211 Genève 4, Switzerland

AND

CHRISTIANE PERRIN AND ROGER CHEVREL

Laboratoire de Chimie Minérale B, Laboratoire Associé au CNRS, No 254, Université de Rennes, Avenue du Général Leclerc, 35000 Rennes, France

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We present a study of the properties of the series $Mo_6X_{8-x}Y_x$ (X = S, Se, Te; Y = Br, I) having the hexagonal rhombohedral structure of the $PbMo_6S_8$ type. For X = S we have found two new superconducting compounds $Mo_6S_6Br_2$ and $Mo_6S_6I_2$, having critical temperatures of 13.8 and 14.0°K, respectively. We further find that Mo_6Te_8 becomes superconducting ($T_c \approx 2.6$°K) upon substitution of Te by small quantities of iodine, and that in the case of Mo_6Se_8 substitution of a Se atom by a halogen, raises T_c up to about 7.6°K.

Introduction

The ternary molybdenum chalcogenides of the type $M_xMo_6X_8$ [M = Cu, Ag, Sn, Pb, ...; X = S, Se, Te] (*1*) are well known for their anomalous superconducting properties (*2, 3*). The two binary compounds, Mo_6Se_8 and Mo_6Te_8, can be obtained by direct synthesis, contrary to Mo_6S_8 which has so far only been produced indirectly by attacking a $M_xMo_6S_8$ compound by hydrochloric acid (*4*). This Mo_6S_8 compound decomposes at 470°C.

The structure of all these compounds contains units of Mo_6X_8, the chalcogens forming a pseudo cube containing a Mo_6 octahedron (*5*). These units are rotated by about 25° around the ternary axis, leaving channels along the rhombohedral axes between the units. The M-elements enters these channels and stabilizes thus Mo_6S_8. One of the purposes of the present work was to stabilize Mo_6S_8 by substituting for sulfur a larger halogen: bromine or iodine.

On the other hand, it has been suggested that superconductivity in these compounds is due to the Mo-4d-electrons, and that electronically one may consider these compounds as being composed of weakly coupled Mo_6X_8 (X = S, Se, Te) units (*3, 6*). Subsequent band calculations for $PbMo_6S_8$ by Anderson, Klose, and Nohl (*7*), and by Mattheiss and Fong (*8*) show that the band structure near the Fermi level is essentially composed of narrow d-bands, corresponding to molecular levels of the Mo_6S_8 unit. The reason for the narrowness of the bands near E_F is the nonbonding $d_{x^2y^2}$ character of the corresponding molecular orbitals. One important result of these calculations is that the sulfur p-band is filled, i.e., sulfur has the valency −2. In the compound

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[*] Permanent address: Laboratoire de Chimie Minérale B, 35000 Rennes, France.

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Mo_6X_8 the position of the Fermi level (or, equivalently the number of d-electrons on the Mo_6-cluster) strongly depends on the valency of the X-atom. We therefore expect that the substitution of the chalcogen by a monovalent atom may change the electronic properties considerably.

Recently a number of new phases were found in the Mo-X-Y system (X = S, Se, Te; Y = Cl, Br, I): $Mo_6X_{10}Y$ (*9*), MoSY (*10*), MoS_2Cl_3, $Mo_3S_7Cl_4$ (*11*, *12*), MoS_2Y_2, and $Mo_2S_5Y_3$ (*13*). In this work we describe the synthesis and the properties of new compounds of the type $Mo_6X_{8-x}X_x$.

Sample Preparation

The samples were prepared by mixing the appropriate amounts of powder of molybdenum, the molybdenum-halide (MoY_2), and the chalcogen X. This mixture was pressed into pellets and reacted at 1050°C for 24 hr. This initial heat treatment was followed by a second one under the same conditions.

For the sulfides the X-ray analysis showed a single phase only for $x = 2$, i.e., for the compounds $Mo_6S_6Br_2$ and $Mo_6S_6I_2$. The lattice parameters of these two compounds are listed in Table I. The results of a chemical analysis are given in Table II. This analysis shows that the two compounds are nonstoichiometric, with a deficiency of halogens. In Table III, we give the calculated and the experimental densities. We did not succeed in synthesizing the compounds $Mo_6S_6Cl_2$.

For the selenides and tellurides it has already been shown that the solid solutions $Mo_6X_{8-x}Y_x$ (X = Se, Te; Y = Br, I) exist for $0 \leqslant x \leqslant 3$ (*9*). In Fig. 1. we show the lattice parameters for these phases.

TABLE II

CHEMICAL ANALYSIS OF $Mo_6S_6Br_2$ AND $Mo_6S_6I_2$—MEASURED AND CALCULATED WEIGHT PERCENTAGES

	Mo	S	Br
Calc. (%)	62.04	20.73	17.22
Meas. (%)	63.5 ± 0.2	21.7 ± 0.2	14.8 ± 0.4
			I
Calc. (%)	56.33	18.83	24.84
Meas. (%)	58.9 ± 0.2	19.3 ± 0.2	21.8 ± 0.4

In all compounds investigated here, the X-ray patterns show a hexagonal–rhombohedral lattice, analogous to the Mo_6Se_8 lattice.

The fact that the sulfides only exist for $x = 2$ strongly suggests that these compounds are ordered with the halogens occupying the 2c-sites on the ternary axis. This assumption can be checked in an investigation presently underway concerning the structure of these compounds. For the selenides and the tellurides the situation is different since the solid solutions exist on both sides of $x = 2$. However, the fact that the variation of the lattice parameters saturates above $x = 2$ may indicate that here also the halogens occupy preferentially the 2c-sites.

Superconducting and Normal State Properties

All these compounds turn out to be conductors with similar resistivities as in the $x = 0$ compounds. Susceptibility measurements at room temperature on $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ yield 0.35×10^{-6} and 0.33×10^{-6} emu/g, respectively, close to the values found for other ternary Mo-chalcogenides.

The superconducting transitions were measured both inductively (400 Hz) and resistively. The transitions were typically 1 to

TABLE I

RHOMBOHEDRAL AND HEXAGONAL LATTICE PARAMETERS OF $Mo_6S_6Br_2$ AND $Mo_6S_6I_2$

Compound	a_R (Å)	α_R°	a_H (Å)	c_H(Å)	V_H (Å^3)
$Mo_6S_6Br_2$	6.503	94.43	9.545	10.357	817.2
$Mo_6S_6I_2$	6.563	94.50	9.639	10.437	840.8

TABLE III

CALCULATED AND MEASURED DENSITY d(g/cm^3), SUSCEPTIBILITY $\chi(10^{-6}$ emu/g) CRITICAL TEMPERATURE T_c[°K] AND INITIAL SLOPE OF THE CRITICAL FIELD VS TEMPERATURE $(dH_{c2}/dT)_{t=t_c}$ [kG/°K] FOR $Mo_6S_6Br_2$ AND $Mo_6S_6I_2$

	d_{calc}	d_{meas}	χ	T_c	dH_{c2}/dT
$Mo_6S_6Br_2$	5.66	5.60	0.35	13.8	—
$Mo_6S_6I_2$	6.06	5.80	0.33	14.0	31

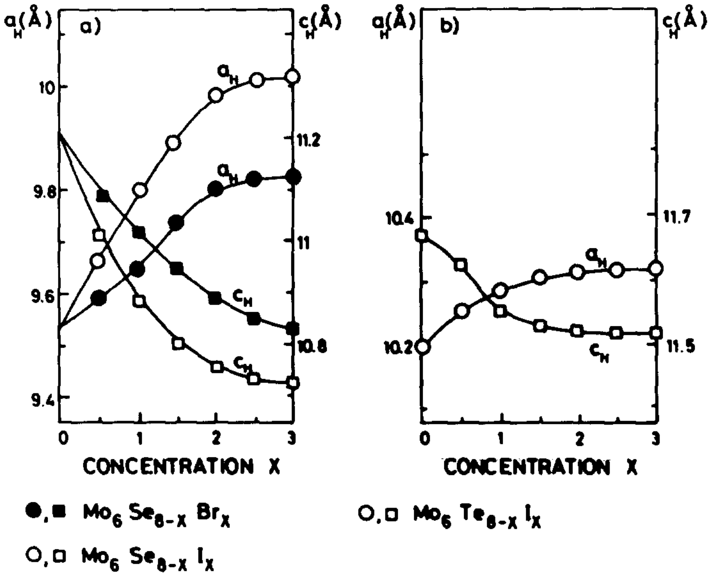

FIG. 1. Hexagonal lattice parameters for the series $Mo_6Se_{8-x}Br_x$, $Mo_6Se_{8-x}I_x$, and $Mo_6Te_{8-x}I_x$.

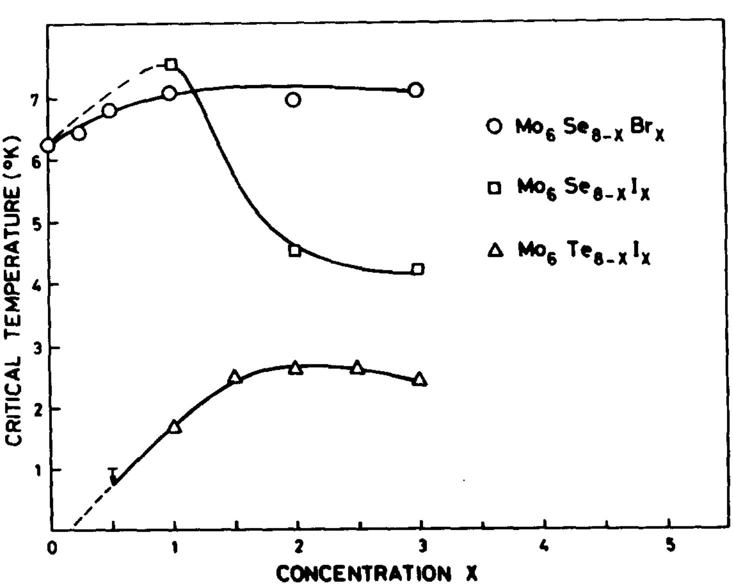

FIG. 2. Critical temperature, T_c, as a function of halogen concentration, x.

2°K broad. These broad transitions may reflect a deficiency or a nonuniform distribution of the halogens. Since the width of the transitions varied somewhat from sample to sample we decided to define T_c by the onset of the transitions. The critical temperatures for $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ was found to be 13.8 and 14.0°K, respectively.

The initial slope of the critical field was measured for $Mo_6S_6I_2$. This measurement also showed broad transitions. Defining H_{c2} by the midpoint of the transition we find $(dH_{c2}/dT)_{T_c} = 31$ kG/°K, 40% below the value found in $PbMo_6S_8$. If we define H_{c2} by the onset of the superconducting state we find $(dH_{c2}/dT)_{T_c} = 50$ kG/°K. The different results obtained for $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ are summarized in Table III.

Substitution of Se by Br or I in Mo_6Se_8 produces an increase in T_c up to 7.1°K for Mo_6Se_7Br and 7.6°K for Mo_6Se_7I. At higher halogen concentrations T_c decreases for $Y = \mathrm{I}$, and saturates around 7°K for $Y = \mathrm{Br}$. Since the transitions in the latter case were large at high bromine concentrations, it might be that the apparent saturation of T_c is a result of inhomogeneous samples.

Mo_6Te_8 is not superconducting above 1°K and so far no compound in this class of materials containing an important quality of tellurium was found to be superconducting. However, substitution of Te by iodine in Mo_6Te_8 makes the compound superconducting with a maximum T_c situated at the compound $Mo_6Te_6I_2$ ($T_c \cong 2.6$°K). In Fig. 2 we show the concentration dependence of T_c.

Discussion

The two bandstructure calculations, mentioned in the Introduction, agree in the gross features of the arrangement of the levels. They also agree in the result that the electron states near the Fermi surface are *d*-like with small bandwidths. These bandwidths are essentially determined by the Mo–Mo intercluster distance $d_{\mathrm{Mo-Mo}}$, a distance we earlier pointed out should play an important role in determining the electronic properties of these phases (*14*).

In what follows we discuss our results in relation to these calculations. Since sulfur is found to have the valency −2 (*7, 8*) there are 20 4*d*- and 5*s*-electrons per unit in the stoichiometric Mo_6S_8 compound. As Pb is probably divalent in $PbMo_6S_8$ (*8*) giving its two 6*p* electrons to the Mo_6 4*d*-bands, there will be 22 electrons on the Mo_6-cluster in stoichiometric $PbMo_6S_8$. Thus the effect of the third element M (in $M_xMo_6S_8$) is not only to push the Mo_6S_8 units apart but also to modify the position of the Fermi level in the 4*d*-band. If, for instance, we substitute Pb by rare-earth (RE) atoms such as La, Gd, or Lu, we observe an important drop in the density of states and in T_c (*3, 6*). This can be qualitatively understood in terms of the bandstructure obtained by Andersen *et al.* (*7*). Since the volume of the hexagonal unit cell decreases when we substitute Pb by La we believe the RE to be trivalent in the $(\mathrm{RE})_xMo_6S_8$ compounds (*6*). The number of *d*-electrons in these compounds is therefore close to 23 for stoichiometric $(\mathrm{RE})Mo_6S_8$ and close to 23.5 for $(\mathrm{RE})_{1.2}Mo_6S_8$. If we assume, according to (*7*) that the Fermi level in $PbMo_6S_8$ is situated near the first maximum in the density of states of the *Eg*-band, we find it near the minimum of the density of states in the $(\mathrm{RE})_xMo_6S_8$.

Turning to the compounds containing halogens, it is clear that the substitution of sulfur by a halogen must change the number of *d*-electrons, i.e., the Fermi level. If we suppose that the *p*-levels remain below E_F, each Br or I atom will add one electron to the *d*-band. Therefore, $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ will have 22 electrons per Mo_6 cluster, exactly as in $PbMo_6S_8$. It is therefore not very surprising that these two compounds turn out to be superconductors. However, the lattice parameters are not the same as in $PbMo_6S_8$. They are actually closer to those of $Cu_2Mo_6S_8$ at room temperature, so that the bandwidths might be different. In fact, the measured susceptibility is about $\frac{2}{3}$ of the one found in

$PbMo_6S_8$, showing that the density of states is probably reduced by some 30–40% in $Mo_6S_6I_2$ as compared to $PbMo_6S_8$. This correlates well with the measured reduction of $(dH_{c2}/dT)_{T_c}$ of about 40%.

The stabilization of Mo_6S_8 by halogens (Br, I) is partly due to the increase in volume, as in the case of the stabilization by Pb, Sn, Ag, etc. We believe, however, that the change in charge transfer is also important for the stability of these phases. In fact all the stable $M_xMo_6S_8$ compounds have 22 or more electrons on the Mo_6-cluster.

The superconducting properties of the selenides and the tellurides are in general rather different from those of the sulfides. It is for instance found that the $(RE)Mo_6Se_8$ (*15*) have higher critical temperatures than $PbMo_6Se_8$. This seems to be contrary to the calculations of Andersen *et al.* (*7*) who predict similar bandstructures for the sulfides, the selenides, and the tellurides. One striking difference between the sulfides, the selenides, and the tellurides is that the X–X distances do not increase proportionally to the ionic radii when going from S to Te. To illustrate this point, we compare the X–X distances in the three Mo_6X_8 compounds (X = S, Se, Te). If we calculate the X radii [in angstroms] from the mean value of these distances in each compound, one finds $r_S = 1.72$, $r_{Se} = 1.78$, and $r_{Te} = 1.89$. The corresponding ionic crystal radii are 1.70, 1.84, and 2.07, respectively (*16*). For sulfur the estimated radius is close to the ionic radius and this makes it plausible that sulfur has valence −2. However, for Se and Te the estimated radii differ considerably from the ionic radii. We may obtain a rough estimate of the charges on the X atoms Q_x by replacing these atoms by uniformly charged spheres and taking the covalent radii as the radii for which $Q_x = 0$. Such an estimate gives $Q_S = -2e$, $Q_{Se} = -1.75e$ and $Q_{Te} = -1.33e$. These estimates indicate that contrary to the result of Ref. (*7*) the *p*-band in Se and Te may possibly cross the Fermi surface. The bandstructure of the selenides and the tellurides near the Fermi surface may therefore be quite different from the one of the sulfides.

The increase in T_c upon substitution of Se by a halogen in Mo_6Se_8 and the appearance of superconductivity in Mo_6Te_8 upon substitution of Te by I is, we believe, mainly a result of the change in the charge transfer. However, if the *p*-levels really cross the Fermi surface a simple estimate of the shift in the Fermi level is not possible.

Finally we think that it is essential that the halogens occupy the 2*c* sites on the ternary axis. In the $M_xMo_6X_{8-x}X'_x$ series, like $PbMo_6S_{8-x}Se_x$ (*14*), one generally observes a sharp drop in T_c when one substitutes one chalcogen by another. The maximum T_c is generally found close to the ternary compound and the minimum T_c is found close to the middle of the series ($x \approx 4$). We believe that this decrease is due to a random distribution of the two chalcogenes on both 6*f* and 2*c* sites. Such a distribution destroys the threefold rotational point symmetry around the ternary axis and this, in particular, removes the twofold degeneracy of the *Eg*-band at the Fermi level.

Conclusion

We have characterized in this work two new superconducting compounds, $Mo_6S_6Br_2$ and $Mo_6S_6I_2$, and we have found superconductivity in the solid solution series $Mo_6Se_{8-x}Br_x$, $Mo_6Se_{8-x}I_x$, and $Mo_6Te_{8-x}I_x$.

All these materials belong to the same structural class as $PbMo_6S_8$. It is worth noting that the two thiohalides $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ have the third highest T_c so far found for a ternary compound, close to the highest value reported for $SnMo_6S_8$ and $PbMo_6S_8$. However, contrary to the latter ones, there are no metal ions in the channels in the thiohalides.

Bandstructure calculations show that the bands in the sulfides are very narrow near the Fermi surface. Since each band contains only fractions of electrons per atom a small change of the valency of the M or X atom in a

$M_x\mathrm{Mo}_6X_8$ compound may change considerably the position of the Fermi level. We believe that this effect of charge transfer is the main reason for the different physical properties of the different $M_x\mathrm{Mo}_6X_8$ compounds. In addition the size of the M and X atoms plays a role in determining the intercluster Mo–Mo distance $d_{\mathrm{Mo-Mo}}$, which to a large extent determines the band width.

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