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# New superconducting ternary molybdenum chalcogenides $InMo_6Se_8$,$TlMo_6S_8$, and $TlMo_6Se_8$

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We present the synthesis and the physical properties of new ternary molybdenum chalcogenides $MMo_6X_8$ ($M=$In, Tl; $X=$S, Se) that cannot be made by the usual high-temperature techniques (except for $InMo_6S_8$). These materials were obtained by diffusion of the ternary element into the binary phase $Mo_6X_8$ at a relatively low temperature (430 °C and 520 °C for the sulfides and selenides, respectively). They crystallize in the rhombohedral space group $R3$ ($C_3^4$) with ($a_r=6.78$ Å, $\alpha_r=89.86°$) when $M=$In and $X=$Se and with ($a_r=6.57$ Å, $\alpha_r=88.45°$) and ($a_r=6.836$ Å, $\alpha_r=88.35°$) when $M=$Tl and $X=$S and Se, respectively. $TlMo_6Se_8$ presents a large temperature-dependent paramagnetism and begins superconducting at 12.2 K, the highest value ever observed in the selenide Chevrel phases, while that of $TlMo_6S_8$ is lower, 8.7 K. The susceptibility of $InMo_6Se_8$ reveals the existence of two first-order transitions that have considerable hysteresis, while only one transition without hysteresis is observed for $InMo_6S_8$. The absence of superconductivity down to 1.5 K has been confirmed for this last compound, while the homolog selenide begins superconducting at 8.2 K.

## INTRODUCTION

The class of molybdenum chalcogenides known variously as ternary molybdenum chalcogenides or as Chevrel phases ($MMo_6X_8$) exhibit a perplexing array of physical properties including superconductivity,[1] extremely high critical magnetic fields,[2] and unusual magnetic properties.[3] This has prompted many experimental studies since the initial report of their characterization in 1971.[4] The characteristic structural feature of these phases[5] is an $Mo_6X_8$ cluster with $X$ atoms approximating a cube and Mo atoms being slightly above the centers of the cube faces. Each cube is rotated approximately 25° about its body diagonal ($\bar{3}$ axis). This arrangement of the $Mo_6X_8$ units leaves large cavities between them. The manner in which the cavities are filled by the $M$ (ternary) atoms depends mainly on the size of the $M$ atoms. Large ternary $M$ atoms sit on the $\bar{3}$ axis, but small ternary atoms occupy tetrahedral sites displaced away from the $\bar{3}$ axis.

So far, over forty elements which are represented by the shaded boxes of Fig. 1 have been reported to form ternary Chevrel phases; most of them are superconducting. A number of possible ternary elements have not been reported to exist in the $MMo_6X_8$ structure type. These include Hg, Tl, and In (in this last case the sulfide but not the selenide is known), as well as other possibilities. We have already reported the preparation of $Hg_xMo_6S_8$ and report here the preparation and properties of $TlMo_6S_8$, $TlMo_6Se_8$, and $InMo_6Se_8$. Attempts to prepare these phases by the usual high-temperature techniques ($T\sim1200$°C) lead to the discovery of both new pseudo-one-dimensional metals $M_2Mo_6X_6$ ($X=$Se, Te, and $M=$In, Tl) (Refs. 6 and 7) and new high-field superconducting compounds $In_xMo_{15}Se_{19}$ (Ref. 8). The structure of the last compound[9] can be viewed as an $InMo_6Se_8$ compound with a modified stacking of units perpendicular to the $c$ axis. A change in the period of the lattice in the $c$ direction but not in the basal plane is similar to a certain extent to what occurs commonly in layer compounds, leading to different polytypes which can be synthesized depending on the heating conditions, temperature of annealing and quenching, etc. The temperature of preparation is also of great importance in obtaining $MMo_6X_8$ ($M=$In, Tl), which we find are not stable at high temperature.

A recent study,[10] leading to the discovery of new Chevrel phases $Hg_xMo_6S_8$ (again unstable at high temperatures) suggested the possibility of inserting ternary elements into the channels of the metastable phase $Mo_6S_8$ at low temperature. We here extend this low-temperature diffusion technique to the synthesis of the known compound $InMo_6S_8$ and unknown ternary molybdenum chalcogenides such as $InMo_6Se_8$, $TlMo_6X_8$ ($X=$S, Se). A major motivation for these investigations has been the possibility of finding high superconducting critical temperatures in such materials. Behavior of the superconducting critical temperature ($T_c$) in the Chevrel phases is, however, not completely understood. Nevertheless, some trends in the magnitude of $T_c$ between different compounds are apparent. Insertion of divalent $M$ cations in $Mo_6S_8$ often yields high $T_c$ values, whereas insertion in the isostructural selenide $Mo_6Se_8$ more often depressed $T_c$. The reverse is observed with trivalent $M$ cations such as in the rare-earth sequence. From crystallographic data,[11] In has been found to be trivalent in $InMo_6S_8$ and should remain trivalent in the selenide. Also, thallium might be expected to be trivalent, since the valence of a given cation is generally the same in both sulfides and selenides and remains the same for other ternary elements belonging to the same column. Based on the previous remarks, new selenide phases with $In^{3+}$ and $Tl^{3+}$ should have high superconducting transition temperatures.

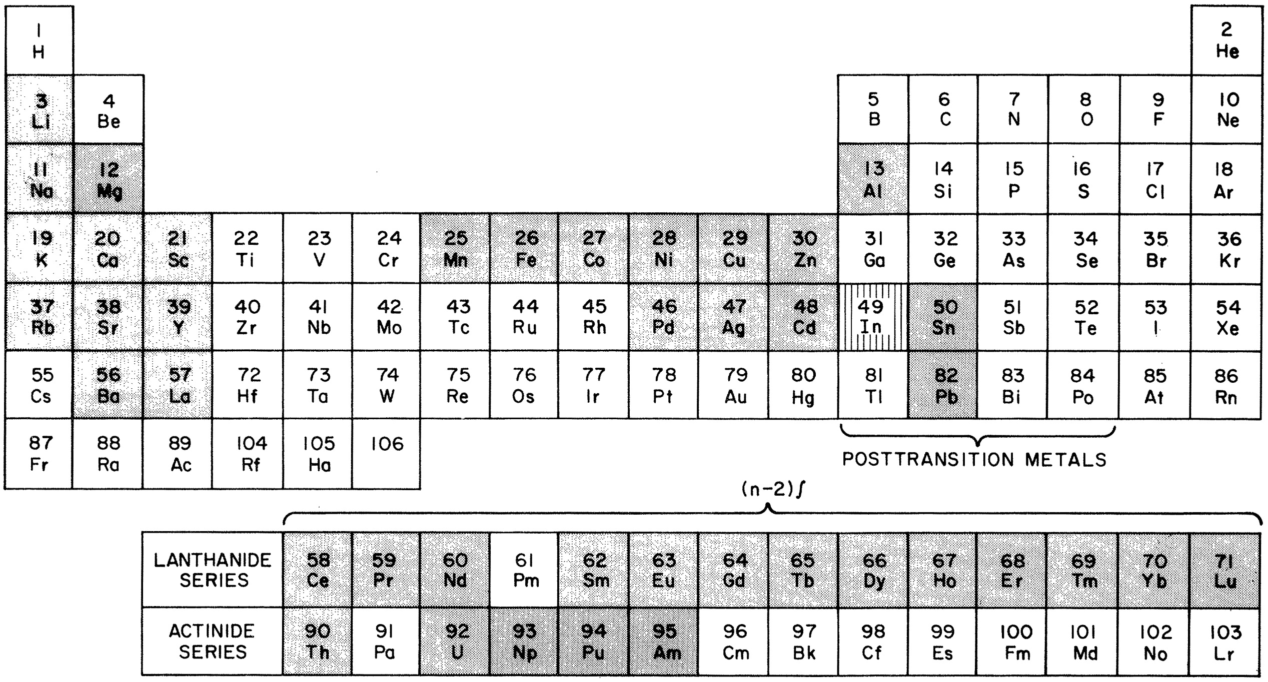

FIG. 1. Elements that have been reported as the ternary element in a Chevrel phase are shaded on the Periodic Table [after Delk (Ref. 27) with some modifications].

In the following, we describe the preparation of the new phases $M_x\mathrm{Mo}_6X_8$ ($M=\mathrm{In}$, Tl and $X=\mathrm{S}$, Se), the measurements of their superconducting critical temperatures, and the measurement as a function of temperature of the magnetic susceptibilities. In the course of the investigation, we also studied the stability of the new materials as well as the effect of going off stoichiometry in the ternary element content.

## SYNTHESIS

The new materials $M_x\mathrm{Mo}_6X_8$ ($M=\mathrm{In}$, Tl; $X=\mathrm{S}$, Se) reported in this paper were obtained by insertion of the ternary element into the channels of the binary phase $\mathrm{Mo}_6X_8$. In contrast to $\mathrm{Mo}_6\mathrm{S}_8$, $\mathrm{Mo}_6\mathrm{Se}_8$ can be formed by direct combination of elements, using the high-temperature technique. From our own experience the $\mathrm{Mo}_6\mathrm{Se}_8$ obtained by this method is always contaminated by $\mathrm{MoSe}_2$. The purer $\mathrm{Mo}_6X_8$ used as starting material in these reactions was prepared according to the following reactions which have been described in detail previously[10] when $X=\mathrm{S}$:

$$2\mathrm{Cu}+6\mathrm{Mo}+8X\rightarrow\mathrm{Cu}_2\mathrm{Mo}_6X_8\ , \qquad (1)$$

$$\mathrm{Cu}_2\mathrm{Mo}_6X_8+\mathrm{I}_2\rightarrow\mathrm{Mo}_6X_8+2\mathrm{CuI}\ . \qquad (2)$$

The copper sulfide and selenide Chevrel phases were synthesized at high temperature from a mixture of elements [reaction (1)] as reported in the literature.[11] The copper was removed by reacting the ternary molybdenum chalcogenide ($\mathrm{Cu}_2\mathrm{Mo}_6X_8$) with an excess solution of iodine in acetonitrile, in sealed quartz ampoules [reaction (2)]. Chemical analysis of the unreacted iodine indicates that a complete oxidation requires more severe conditions for the selenide (4 d at 80 °C) than for the sulfides (2 d at 50 °C). Atomic absorption analysis of both $\mathrm{Mo}_6\mathrm{S}_8$ and $\mathrm{Mo}_6\mathrm{Se}_8$, which showed less than 0.03% and 0.05% Cu by weight, respectively, confirm the quantitative reaction. X-ray studies of the resulting product $\mathrm{Mo}_6\mathrm{X}_8$ ($X=\mathrm{S}$, Se) indicate a single phase with lattice parameters similar to the ones reported in the literature[13,14] (Table I).

The ternary phase is produced by reacting the appropriate amounts of the pure binary phase $\mathrm{Mo}_6X_8$ and ternary element $M$:

$$\mathrm{Mo}_6X_8(X=\mathrm{S},\ \mathrm{Se})+M\rightarrow M\mathrm{Mo}_6X_8\ . \qquad (3)$$

Indium power or Tl in the form of lumps was placed in a silica tube, degased and sealed under vacuum. When $M=\mathrm{Tl}$, all manipulations were carried out in a glove box under argon atmosphere. The samples are reacted at 420 °C and 520 °C for the sulfides and selenides, respectively. Reaction times of one week when $M=\mathrm{In}$ and three weeks when $M=\mathrm{Tl}$ were necessary in order to obtain single-phase samples. These new compounds are black and are stable in air.

Thermal stability of these new phases was determined by annealing at different temperatures. $\mathrm{InMo}_6\mathrm{Se}_8$ is stable up to 550 °C; at higher temperatures x-ray studies show the presence of extra peaks similar to those reported by Chevrel for $\mathrm{In}_x\mathrm{Mo}_{15}\mathrm{Se}_{19}$. The formation of this phase can be explained by writing a reaction such as

$$2.75\mathrm{InMo}_6\mathrm{Se}_8\rightarrow\mathrm{In}_{2.75}\mathrm{Mo}_{15}\mathrm{Se}_{19}+1.5\mathrm{MoSe}_2\ , \qquad (4)$$

where $\mathrm{In}_{2.75}\mathrm{Mo}_{15}\mathrm{Se}_{19}$ lies in the homogeneity range previously reported. Both of the thallium compounds decom-

TABLE I. Lattice parameters for the Chevrel phases $M_xMo_6X_8$ ($M$=In, Tl; $X$=S, Se) and of several previously reported Chevrel phases are given in both the rhombohedral and hexagonal systems along with the hexagonal unit-cell volume.

| Compounds | $a_r$ | $\alpha_r$ | $a_H$ | $c_H$ | $V_H$ | $T_c$ | $\Delta T_c$ | Reference |
|---|---|---|---|---|---|---|---|---|
| $Mo_6S_8$ | 6.429 | 91.155 | 9.183 | 10.909 | 796.68 | 1.85 | 1.85−1.60 | this work |
| | 6.43 | 91.34 | 9.20 | 10.88 | 797.50 | 1.7 | | 13 |
| $Al_{1.3}Mo_6S_8$ | 6.48 | 95.83 | 9.62 | 10.02 | 803.0 | | | 15 |
| $InMo_6S_8$ | 6.519 | 93.189 | 9.472 | 10.644 | 827.11 | <0.6 | | this work |
| | 6.52 | 92.96 | 9.460 | 10.680 | 827.7 | no | | 12—14,16 |
| $TlMo_6S_8$ | 6.574 | 88.456 | 9.17 | 11.689 | 851.32 | 8.7 | 8.7−6.2 | |
| $LaMo_6S_8$ | 6.51 | 88.90 | 9.12 | 11.48 | 826.9 | 7.1 | | 17,18 |
| $Mo_6Se_8$ | 6.66 | 91.451 | 9.537 | 11.239 | 885.36 | 6.5 | 6.5−6.0 | this work |
| | 6.66 | 91.58 | 9.54 | 11.210 | 889.20 | 6.2 | | 14 |
| $InMo_6Se_8$ | 6.786 | 89.860 | 9.585 | 11.782 | 937.48 | 8.1 | 8.1−7.3 | |
| $TlMo_6Se_8$ | 6.836 | 88.345 | 9.526 | 12.177 | 957.185 | 12.2 | 12.2−11.3 | |
| $LaMo_6Se_8$ | 6.80 | 88.96 | 9.52 | 12.00 | 941.80 | 11.4 | | 17,18 |

posed above 550 °C, leading to a mixture of $Tl_2Mo_9S_{11}$ and unknown phases or to a two-phase product ($Tl_2Mo_6Se_6$ and $MoSe_2$) for the sulfides and selenides, respectively. In all these cases complete decomposition was obtained after heating at 1100 °C for about 2 days.

## RESULTS AND DISCUSSION

The powder-diffraction diagrams using Cu$K\alpha_1$ radiation (Fig. 2) of the new compounds $M_xMo_6X_8$ ($X$=S, Se) when $M$=In and Tl, reveal the existence of a single-phase material for a value of $x$ close to 1. Much deviation from this composition as we will see results in two-phase products. The x-ray powder-diffraction patterns of these new materials were indexed by analogy to that of $InMo_6S_8$ on the basis of a hexagonal cell or equivalently a rhombohedral cell. For each compound the lattice parameters obtained by a least-squares fitting of the diffraction peaks are summarized in Table I. A comparison of the observed and calculated $d$ spacings is given in Table II.

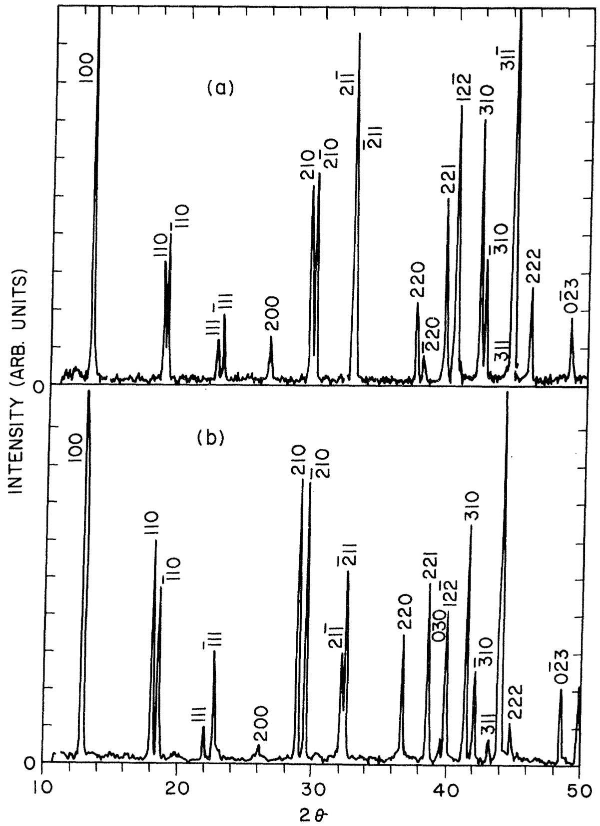

FIG. 2. X-ray powder-diffraction pattern using copper $K\alpha_1$ radiation is shown for (a) $InMo_6Se_8$ and (b) $TlMo_6Se_8$.

The hexagonal $a_H$ lattice parameter decreases while the $c_H$ lattice parameter increases as we go from Al to In and then to Tl. Presumably, the metal is in 3+ oxidation state as previously suggested for group-III*a* elements (Refs. 12, 15, and 16). It is interesting to note that the value of $\alpha_r \approx 90°$ for $InMo_6Se_8$ is significantly lower than the one found for $InMo_6S_8$ (~93°). This result is totally unexpected. It was previously observed that for a given cation the degree of displacement of the ternary element from the $\bar{3}$ axis (which is reflected in $\alpha_r$) is about the same in both the sulfide and the selenide.[12] A final point to note from Table I is the large hexagonal unit-cell volume found for $TlMo_6Se_8$, the largest one ever reported for selenide Chevrel phases. This value is of great interest since a correlation has been pointed out between the volume and $T_c$ by Marezio *et al.*,[5] when comparing $PbMo_6S_8$, $SnMo_6S_8$, $Cu_2Mo_6S_8$, and $AgMo_6S_8$, and by Johnston and Shelton[17] in the rare-earth sequences Re $^{3+}Mo_6X_8$ ($X$=S, Se) where both volume and $T_c$ decrease when going from La to Lu. On this last basis, assuming the oxidation state of Tl to be 3+, we would expect a higher superconducting critical temperature for $TlMo_6Se_8$ than for $LaMo_6Se_8$.[17,18]

The superconducting critical temperature has been determined by using an ac mutual inductance apparatus. The $T_c$ value was defined as the onset of the superconducting critical temperature. The width of the transition is the temperature difference between $T_c$ and a second point obtained by the intersection of the tangent to the inductively measured transition with the baseline where the transition is 100% complete. The results are shown in

TABLE II. The observed $d$ spacings and intensities of the x-ray powder-diffraction patterns using copper $K\alpha_1$ radiation of $InMo_6Se_8$, $TlMo_6Se_8$, and $TlMo_6S_8$ are compared to the values calculated from the lattice parameters of Table I (the Miller indices are based on a rhombohedral cell).

| | $InMo_6Se_8$ | | | $TlMo_6Se_8$ | | | $TlMo_6S_8$ | |
|---|---|---|---|---|---|---|---|---|
| *hkl* | $d_{obs}$ | $d_{cal}$ | *hkl* | $d_{obs}$ | $d_{cal}$ | *hkl* | $d_{obs}$ | $d_{cal}$ |
| 100 | 6.788 | 6.780 | 100 | 6.841 | 6.830 | 100 | 6.576 | 6.570 |
| 110 | 4.833 | 4.830 | 110 | 4.892 | 4.889 | 110 | 4.691 | 4.696 |
| $\bar{1}10$ | 4.759 | 4.759 | $\bar{1}10$ | 4.772 | 4.772 | $\bar{1}10$ | 4.601 | 4.597 |
| 111 | 3.979 | 3.974 | 111 | 4.036 | 4.042 | 111 | 3.879 | 3.877 |
| $\bar{1}11$ | 3.897 | 3.895 | $\bar{1}11$ | 3.912 | 3.911 | $\bar{1}11$ | 3.766 | 3.766 |
| | | | 200 | 3.416 | 3.418 | | | |
| 200 | 3.391 | 3.390 | 210 | 3.084 | 3.084 | 120 | 2.966 | 2.963 |
| 210 | 3.050 | 3.050 | $\bar{2}10$ | 3.025 | 3.025 | $\bar{1}20$ | 2.915 | 2.913 |
| $\bar{2}10$ | 3.014 | 3.014 | $21\bar{1}$ | 2.777 | 2.777 | $\bar{1}21$ | 2.673 | 2.672 |
| $21\bar{1}$ | 2.761 | 2.761 | $\bar{2}11$ | 2.755 | 2.755 | $\bar{2}11$ | 2.653 | 2.654 |
| $\bar{2}11$ | 2.747 | 2.748 | 220 | 2.444 | 2.444 | 220 | 2.349 | 2.348 |
| 220 | 2.415 | 2.415 | 221 | 2.327 | 2.327 | 221 | 2.232 | 2.233 |
| $\bar{2}20$ | 2.379 | 2.379 | 030 | 2.275 | 2.276 | $\bar{2}21$ | 2.169 | 2.169 |
| 221 | 2.290 | 2.290 | $12\bar{2}$ | 2.252 | 2.252 | 130 | 2.091 | 2.091 |
| 030 | 2.259 | 2.260 | 310 | 2.175 | 2.175 | $\bar{1}30$ | 2.065 | 2.064 |
| | | | 311 | 2.092 | 2.092 | | | |
| $12\bar{2}$ | 2.246 | 2.245 | $\bar{1}31$ | 2.055 | 2.054 | $\bar{1}31$ | 1.977 | 1.977 |
| 310 | 2.153 | 2.153 | 222 | 2.021 | 2.021 | $\bar{2}30$ | 1.804 | 1.804 |
| $\bar{3}10$ | 2.134 | 2.134 | $\bar{2}30$ | 1.873 | 1.873 | $\bar{3}21$ | 1.758 | 1.758 |
| 311 | 2.075 | 2.075 | | | | | | |
| $31\bar{1}$ | 2.042 | 2.041 | $\bar{3}21$ | 1.828 | 1.828 | $\bar{2}31$ | 1.743 | 1.742 |
| 222 | 1.985 | 1.984 | | | | | | |
| $0\bar{2}3$ | 1.867 | 1.867 | $\bar{2}31$ | 1.809 | 1.809 | $\bar{1}41$ | 1.546 | 1.546 |
| $32\bar{1}$ | 1.814 | 1.814 | 232 | 1.694 | 1.695 | 240 | 1.480 | 1.481 |
| $\bar{2}31$ | 1.802 | 1.802 | 140 | 1.666 | 1.666 | 340 | 1.327 | 1.327 |
| 040 | 1.694 | 1.695 | $\bar{1}40$ | 1.647 | 1.647 | | | |
| 140 | 1.650 | 1.650 | $\bar{1}41$ | 1.607 | 1.607 | | | |
| 330 | 1.610 | 1.610 | $\bar{3}30$ | 1.589 | 1.590 | | | |
| $\bar{1}14$ | 1.596 | 1.596 | 240 | 1.542 | 1.542 | | | |
| $\bar{3}30$ | 1.587 | 1.586 | 340 | 1.382 | 1.382 | | | |
| 420 | 1.524 | 1.525 | $\bar{4}22$ | 1.377 | 1.377 | | | |
| $\bar{4}21$ | 1.469 | 1.469 | | | | | | |
| $\bar{3}\bar{3}2$ | 1.442 | 1.442 | | | | | | |
| $\bar{4}22$ | 1.374 | 1.374 | | | | | | |
| 340 | 1.365 | 1.365 | | | | | | |
| 050 | 1.356 | 1.356 | | | | | | |
| $\bar{4}\bar{3}2$ | 1.257 | 1.257 | | | | | | |
| $\bar{4}32$ | 1.250 | 1.250 | | | | | | |

Table III. All the new compounds are superconducting. $TlMo_6Se_8$ has the highest superconducting critical temperature ever reported for selenide Chevrel phases, while $InMo_6S_8$ as previously reported[12] does not superconduct above 1 K. It is clear from the compounds investigated here that $T_c$ can be related to the volume, since, for example, both $TlMo_6S_8$ and $TlMo_6Se_8$, which have a greater unit-cell volume than $LaMo_6S_8$ and $LaMo_6Se_8$, respectively, also have higher $T_c$. The absence of $T_c$ down to 1 K for $InMo_6S_8$ which has the same unit-cell volume as $LaMo_6S_8$, for which $T_c \sim 7$ K, appears to invalidate this empirical observation. We will shortly explain this apparent contradiction.

The magnetic susceptibilities of the new materials reported here were measured from $T_c$ to room temperature using the Faraday technique. In all cases, the observed susceptibilities (solid curves in Fig. 3) show a Curie-type tail at low temperature due to the presence of magnetic impurities. The low-temperature data can be fitted to Eq. (5):

$$\chi_g = \frac{C_g}{(T+\Theta)} + \chi_0 , \tag{5}$$

where $C_g$, $\Theta$, and $\chi_0$ are assumed to be constant at sufficiently low temperature. The results of this fit are summarized in Table IV. The diamagntic contribution of the individual atomic cores can be subtracted from $\chi_0$ to obtain the net paramagnetic contribution $\chi_{para}$ (Table IV). $TlMo_6Se_8$ has the largest $\chi_{para}$ and the highest $T_c$, while

TABLE III. The superconducting transition temperature and transition widths are given for a number of Chevrel phases and compared to the hexagonal unit-cell volume.

| Compounds | $T_c$ (K) | $\Delta T_c$ | $V_H$ (Å$^3$) |
|---|---|---|---|
| $InMo_6S_8$ | 1 | | 827.7 |
| $TlMo_6S_8$ | 8.7 | 8.7−6.2 | 851.9 |
| $LaMo_6S_8$[a] | 7.1 | | 826.9 |
| $InMo_6Se_8$ | 8.1 | 8.1−7.3 | 937.48 |
| $TlMo_6Se_8$ | 12.2 | 12.2−11.3 | 957.1 |
| $LaMo_6Se_8$[a] | 11.4 | | 941.8 |

[a]References 17 and 18.

those with lower $\chi_{para}$ have correspondingly lower $T_c$. Previous workers have suggested that the $T_c$ of the Chevrel phases increases with an increasing density of states at the Fermi level,[11] but the magnetic data here cannot be so easily interpreted, since $\chi_{para}$ is due to the sum of several contributions, only one of which is proportional to the density of states.

Turning back to the magnetic data, at higher temperature we assume that $C_g$ and $\Theta$ remain constant and that $\chi_0$ is temperature dependent. We show $\chi = \chi_{meas} - C_g/(T+\Theta)$ in Figs. 4, 5, and 6, which represent the susceptibilities corrected for the Curie tail.

Temperature-dependent magnetic susceptibilities in metallic transition-metal compounds are usually ascribed to a temperature dependence of the Pauli paramagnetism (we are not considering compounds that have localized atomic magnetic moments). This results from sharp structure in the density of states at the Fermi level over an energy interval of $\sim 2kT$. Andersen, Klose, and Nohl[19] performed band-structure calculations for several of these ternary molybdenum chalcogenides. They find near the Fermi level two partially filled bands—a broad $A_{1g}$ band (composed mainly of Mo $d_z^2$ orbitals) and a much narrower $E_g$ band (composed of $d_{xy}$ and $d_x^2$-$d_y^2$ orbitals), which has two van Hove singularities. It has been suggested that the temperature dependence of the susceptibility of $PbMo_6S_8$ (Ref. 20) and of $LaMo_6Se_8$ (Ref. 17) are due to the peaks in the density of states at these singularities (and consequently that the Fermi level falls very close to these peaks). It seems to us that this kind of explanation for the temperature dependence of the susceptibility reported for the above compounds and presently observed for $TlMo_6Se_8$ may not be the only possibility. For this explanation to be correct in the temperature range of measurement, changes in the density of states on the order of 50% must occur for energy differences as small as a few mRy near the Fermi level. In this model for a temperature-dependent susceptibility, the deviation of the susceptibility from a constant value should increase as the square of the temperature.[21] The behavior observed here is more complicated.

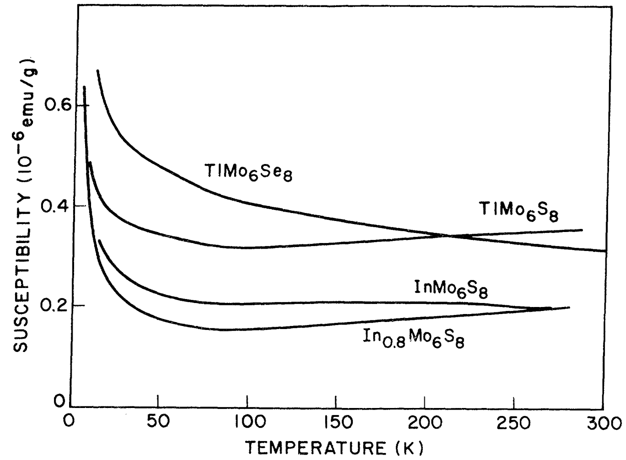

FIG. 3. Observed magnetic susceptibility of the new materials as a function of temperature.

This kind of sharp structure in the density of states has been invoked to explain temperature-dependent susceptibilities at low temperatures for a number of other types of compounds such as the metallic layered transition-metal dichalcogenides[22] and the superconducting $A15$ compounds,[23] which have some similar properties—especially large electron-phonon coupling and incipient structural instabilities. Although in lowest-order perturbation theory the electron-phonon coupling does not affect the magnetic susceptibility,[24] we suggest that in strongly coupled systems the magnetic susceptibility is affected. We are not aware, however, of any theory which can directly be applied to this problem to test our conjecture.

When $M = $ In, for both sulfides and selenides the susceptibility behavior is peculiar. As can be seen from Fig. 5 the susceptibility of $InMo_6Se_8$ reveals the existence of

TABLE IV. The parameters obtained from a fit of the low-temperature data to the Curie-Weiss law are given for the compounds $M_xMo_6X_8$ ($M$=In, Tl; $X$=S, Se). Shown are the temperature intervals over which the fit was determined, the Weiss constant $\Theta$, the temperature-independent susceptibility $\chi_0$, $\chi_{para}$ obtained from $\chi_0$ after the core diamagnetism has been substracted out, and finally the superconducting temperature $T_c$.

| Compounds | Interval−fit (K) | $\Theta_p$ (K) | $\chi_0$ ($10^{-6}$ emu/g | $\chi_c$ ($10^{-6}$ emu/g) | $\chi_{para}$ ($10^{-6}$ emu/g) | $T_c$ (K) |
|---|---|---|---|---|---|---|
| $TlMo_6S_8$ | 10−25 | −0.5 | 0.326 | −0.363 | 0.689 | 8.7 |
| $TlMo_6Se_8$ | 12−25 | 2 | 0.420 | −0.323 | 0.743 | 12.2 |
| $InMo_6Se_8$ | 10−25 | 1.5 | 0.370 | −0.330 | 0.700 | 8.1 |
| $InMo_6S_8$ | 5−50 | 2.5 | 0.172 | −0.373 | 0.545 | <1 |
| $In_{0.8}Mo_6S_8$ | 5−50 | 1 | 0.132 | −0.369 | 0.501 | <1 |

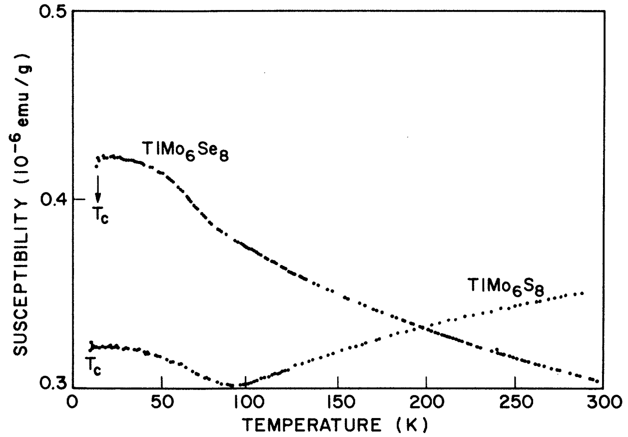

FIG. 4. Susceptibility temperature is shown for both $TlMo_6S_8$ and $TlMo_6Se_8$ when the Curie contribution has been substracted out (see text).

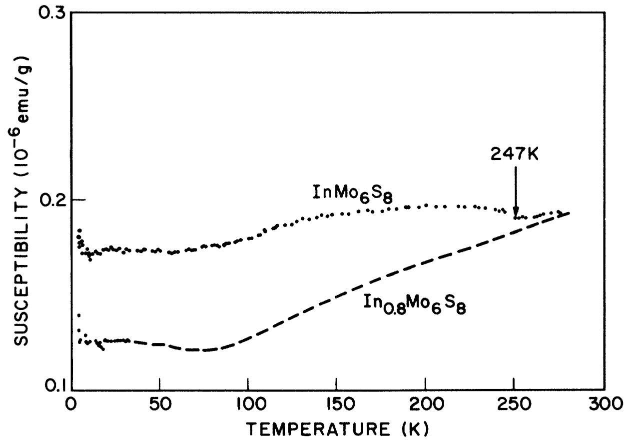

FIG. 6. Susceptibility of $In_xMo_6S_8$ with the Curie contribution substracted out is shown for the nominal compositions $x = 0.8$ and 1.0. The arrow shows the onset of a phase transition.

two first-order transitions that have considerable hysteresis. The upper phase transition occurs at 245 K on cooling and 410 K on warming, and the respective values for the lower transition are 65 and 140 K. In an attempt to learn more about the nature of these anomalies, room-temperature x-ray diffraction diagrams were collected along the higher hysteresis loop at positions marked by numbers (1, 2, and 3) in Fig. 5. The pattern (2) obtained at 300 K after warming the sample from helium temperature is very complex and shows the existence of at least two phases, which disappear by heating past the higher transition temperature. After a complete cycle the final product (3) shows the same diffraction diagram as the starting material (1). This clearly indicates the presence of a multiphase product at low temperature, but inductive measurements on bulk samples show only one superconducting transition at 8.2 K. These results are similar to the ones reported for $Cu_xMo_6X_8$ (Refs. 11 and 25) where, depending on $x$, two low-temperature phases exist. We attempted to prepare $In_xMo_6Se_8$ samples in the range of $0.8 < x < 2$ in order to determine the effect of nonstoichiometry on the lattice-transformation temperature. X-ray studies indicate a narrow homogeneity range for the In phase (with $x \sim 1$), since we observed the presence of $Mo_6Se_8$ in samples for which $x$ was lower than 1 and traces of $In_xMo_{15}Se_{19}$, for $x$ higher than 1.1. The high-temperature phase of $InMo_6Se_8$ probably transforms into two low-temperature phases corresponding either to a different ordering of In ions or to different In concentrations as in the $Cu_xMo_6X_8$ system. Low-temperature x-ray studies may distinguish between these two possibilities.

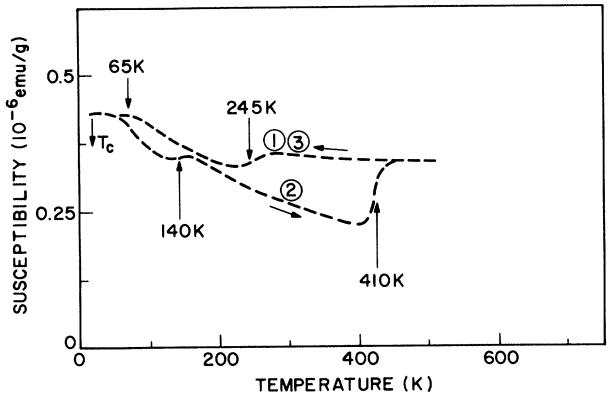

FIG. 5. Temperature-dependent susceptibility of $InMo_6Se_8$ is given after the Curie contribution has been substracted out (see text). The vertical arrows exhibit the onset of a phase transition, while the horizontal arrows distinguish between cooling or warming of the sample.

Magnetic data on $InMo_6S_8$ (Fig. 6) exhibit a slight anomaly in susceptibility near 250 K. Furthermore, at the same temperature, differential-scanning-calorimetry (DSC) measurements show an endothermic peak (Fig. 7). Both of these measurements suggest that temperature-induced lattice distortions occur in $InMo_6S_8$. The final proof for the onset of a structural instability is given by low-temperature x-ray diffractometry. A well-defined splitting of most of the x-ray reflections of the rhombohedral phase occurs below 250 K. A general observation is that the rhombohedral reflections having sixfold multiplicity such as 011 or 010, split into three distinct nonequivalent lines having twofold multiplicity, where as those having twofold multiplicity such as 111 or 222 remain sharp. Based on the above findings, the low-temperature phase has been indexed completely on the basis of a triclinic cell. The cell parameters reported in Table V indicate that the volume change is very small at the phase change. A similar distortion from rhombohedral to triclinic leading to the same evolution of the lattice parameters has been recently reported for both $EuMo_6S_8$ and $BaMo_6S_8$ by Baillif *et al.*[26] These authors suppose that this distortion, due to a Jahn-Teller—type electronic instability, is the main reason for the absence of superconductivity in these compounds, since, under pressure, the phase distortion can be suppressed and superconductivity appears. In an attempt to prevent the phase change in $InMo_6S_8$, we attempted to change the

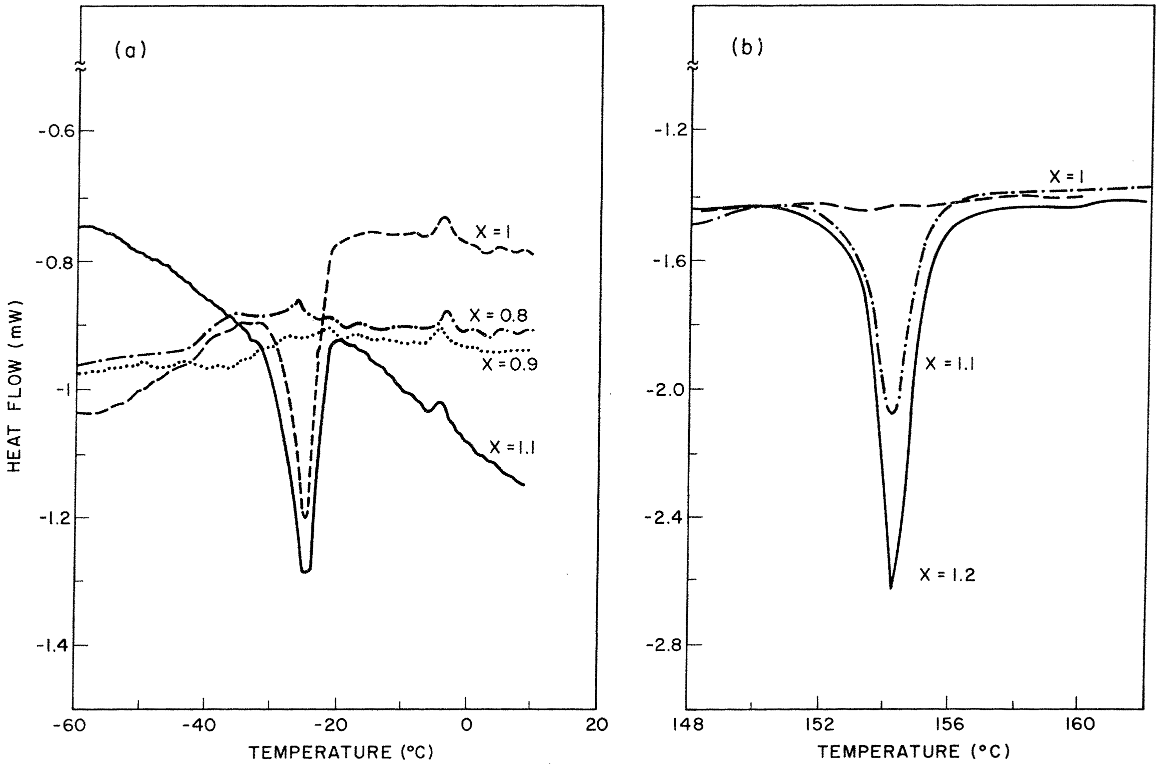

FIG. 7. DSC measurements of the series $In_xMo_6S_8$ for various indium concentrations (a) below room temperature and (b) above room temperature.

stoichiometry of the ternary element. The results of x-ray studies on $In_xMo_6S_8$ samples with $x$ ranging from 0.8 to 1.2 are summarized in Table V. As can be seen for $x$ higher than 1, the lattice parameters remained constant, where as they change for $x$ lower than 1, as in the $Hg_xMo_6S_8$ series,[10] $a_H$ and $V_H$ decrease with $x$ while $c_H$ remains roughly constant. In the present case, $x=0.9$ seems to be the lower limit of the homogeneity range. The $In_{0.8}Mo_6S_8$ sample is both contaminated by traces of $Mo_6S_8$ and shows broad diffraction peaks while $In_{1.2}Mo_6S_8$ appears to be a single phase by x ray. However, it is not single phase, since DSC measurements, which exhibit an endothermic peak near 156 °C (melting point of In), clearly indicate the presence of free indium in samples for $x > 1$ (Fig. 7). The value of $x$ does not exceed 1 in $InMo_6S_8$, which nevertheless has a large rhombohedral angle. The most surprising result comes from the low-temperature DSC measurements (Fig. 7), which indicates the absence of the endothermic peak at $-25$ °C for samples corresponding to nominal values of $x$ lower than 1, while a well-defined peak due to the phase transition is observed for $x$ nominally greater than 1. Furthermore, as can be seen from Fig. 6, the magnetic data exhibit similar behavior, since the anomaly in susceptibility observed near 250 K vanishes as we go from $x=1$ to $x=0.8$. Both measurements seem to suggest that nonstoichiometry (In

TABLE V. Crystallographic parameters as a function of composition in the series $In_xMo_6S_8$ and at low temperature ($\sim 100$ K) for $InMo_6S_8$.

| Compounds | $a_r$ (Å) | $\alpha_r$ (deg) | $a_H$ (Å) | $c_H$ (Å) | $V_H$ (Å$^3$) | | Impurity Phase |
|---|---|---|---|---|---|---|---|
| $In_{1.2}Mo_6S_8$ | 6.518 | 93.15 | 9.467 | 10.652 | 826.85 | $V_R=275.2$ | none |
| $In_{1.1}Mo_6S_8$ | 6.518 | 93.16 | 9.470 | 10.692 | 826.73 | | none |
| $In_1Mo_6S_8$ | 6.516 | 93.15 | 9.464 | 10.697 | 826.07 | | none |
| $In_{0.9}Mo_6S_8$ | 6.512 | 93.13 | 9.457 | 10.696 | 824.61 | | none |
| $In_{0.8}Mo_6S_8$ | 6.506 | 93.12 | 9.447 | 10.640 | 822.35 | | $Mo_6S_8$ plus broad lines |
| Triclinic | | | | | | $V_T=273.9$ | |
| $InMo_6S_8$ | $a$ | $b$ | $c$ | $\alpha$ | $\beta$ | $\gamma$ | $T_c$ |
| Low Temp. | 6.492 | 6.534 | 6.500 | 93.55 | 91.34 | 94.40 | $<1$ K |

in deficiency) suppresses the phase distortion. Still, however, there was no superconductivity above 1 K in $x<1$ samples. It may be that by lowering $x$ we produce an increasing disorder of the In ions in the rhombohedral crystal structure (as suggested by broad diffraction reflections), which will lead to a broad phase transition spread over a large temperature range instead of a sharp one as was observed on $\mathrm{InMo_6S_8}$. This would be consistent with the apparent absence of both the DSC peak and superconductivity.

## SUMMARY

We have reported the preparation of new ternary phases with group-IIIa elements ($M=\mathrm{In}$, Tl) by diffusion into the channels of the binary phase of $\mathrm{Mo}_6X_8$ ($X=\mathrm{S}$, Se) at low temperature, yielding new ternary molybdenum chalcogenides $\mathrm{InMo_6Se_8}$, $\mathrm{TlMo_6S_8}$, and $\mathrm{TlMo_6Se_8}$, which are not stable above 550 °C. From a study of the nonstoichiometry in the ternary element in these compounds, we showed by x-ray diffraction and DSC measurements that even with small size ions ($\mathrm{In}^{3+}$ or $\mathrm{Tl}^{3+}$ ionic radius of 0.81 and 0.93 Å, respectively), the $M_x\mathrm{Mo}_6X_8$ phases allow very little homogeneity range. A single phase is formed only when $x=1$, except for $\mathrm{In}_x\mathrm{Mo_6S_8}$, for which the value of $x$ is found to be $0.9<x<1.0$. $\mathrm{TlMo_6Se_8}$ superconducts at 12.2 K, the highest value of $T_c$ ever reported for the selenide Chevrel phase. When $M=\mathrm{In}$, lattice instabilities occur, which are perhaps linked to the particular type of site occupied by the $M$ cations in the channels of $\mathrm{Mo}_6X_8$.

For compounds having both a rhombohedral angle greater than 93° and more than one $M$ cation per $\mathrm{Mo_6S_8}$ unit (such as Cu, Fe, Co, Zn, etc.), it has been suggested by Yvon[12] that low-temperature phase changes reflect an ordering of the $M$ cations, which in the high-temperature phase are "delocalized" over two sets of sites displaced from the $\bar{3}$ axis. This ordering leads to a distortion of the chalcogen network, which causes a triclinic deformation of the $\mathrm{Mo_6}$ octahedron. In $\mathrm{InMo_6S_8}$, which contains only one atom per $\mathrm{Mo_6S_8}$, the triclinic distortion cannot be due to a similar off-axis ordering of the cations and has a different origin. Presumably this phase change is of the same nature as that which occurs in $\mathrm{EuMo_6S_8}$,[26] and is due to a Jahn-Teller–type electronically driven distortion of the doubly degenerate, $\frac{3}{4}$ filled $e_g$ band (23 electrons). For $\mathrm{InMo_6Se_8}$ the two low-temperature phase transformations observed may reflect different ordering arrangements of the In ions in the channels, which in turn may be related to a possible valence transition between $\mathrm{In}^{+}$ and $\mathrm{In}^{3+}$ with temperature. A more certain knowledge of the oxidation state of indium in these compounds will be of great importance for the understanding of both the temperature-induced lattice instabilities and the large change in $\alpha_r$ between the indium sulfide and selenide Chevrel phases.

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