Bonding in $Mo_{4.5}Ru_{1.5}Te_8$, $Ni_{0.85}Mo_6Te_8$, Chevrel Phase, and Related Compounds

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The nature of bonding in some tellurium analogues of Chevrel and related phases is discussed in detail for the first time. The electronic effect, which is a characteristic feature of bonding in sulfides and selenides of this type, has been found not to occur in the closely related tellurides. A reason for this is suggested. Previously unrecognized features of bonding in Chevrel phase sulfides and selenides, and in $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$, are also reported. The bonding characteristics of compounds containing Mo_6 units are shown to be different from the characteristics of those containing $Mo_{6-x}M'_x$ (M' = Ru, Rh, Re) clusters where the cluster metal M' polarizes the chalcogen valence electrons. Cluster metal oxidation states have been found to influence both intra- and intercluster metal–chalcogen separations in a systematic and predictable fashion. © 1994 Academic Press, Inc.

INTRODUCTION

The Chevrel phases, $M_xMo_6X_8$, and the closely related compounds of composition $Mo_{6-x}M'_xX_8$ (M = metal, M' = Ru, Re, X = S, Se) have attracted considerable interest because of their unusual physical properties (1). For example, many of these compounds are superconductors with large critical magnetic fields (1). Although a large number of Chevrel phase sulfides and selenides have been described, little is known of the tellurium-containing analogues (1).

We have recently reported on the synthesis (2) and ^{125}Te Mössbauer spectra (3) of compounds of the type $Mo_{6-x}M'_xTe_8$ (M' = Ru, Rh) and have also given a detailed structural description (4) of $Mo_{4.5}Ru_{1.5}Te_8$. This structural study of $Mo_{4.5}Ru_{1.5}Te_8$ and a single-crystal X-ray crystallographic description (5) of $Ni_{0.85}Mo_6Te_8$ are the only detailed structural investigations of tellurium-containing analogues of solids related to the Chevrel phase compounds. We have now used the data from the two structural studies (4, 5) to examine the nature of bonding in tellurium-con-

taining analogues of the Chevrel phase compounds. We report here on some fundamental differences between the nature of bonding in the Chevrel phase tellurides and that in the related sulfides and selenides. We also report on how published interatomic distances for the Chevrel phase sulfides and selenides and the compounds $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$, together with some related materials, demonstrate previously unrecognized features of bonding in these compounds. We also describe differences in the bonding properties of compounds containing clusters of composition Mo_6 and $Mo_{6-x}M'_x$.

The discussion of the work reported here requires a brief description of the essential structural characteristics and the models that have been used to explain the bonding properties in the Chevrel phase and related compounds. The binary molybdenum chalcogenides of composition Mo_6X_8 (X = S, Se, Te) have structures based on the stacking of the Mo_6X_8 units. The Mo_6X_8 unit consists of an Mo_6 trigonal antiprism surrounded by eight chalcogens arranged in a distorted cube (Fig. 1). The molybdenum atoms occupy positions close to, but just outside, the faces of the chalcogen cube and the Mo_6X_8 unit is slightly elongated along the hexagonal c axis. Each Mo_6X_8 unit has two chalcogen sites, the axial chalcogen sites designated $X(2)$ which lie along the c axis, and the peripheral chalcogen sites designated $X(1)$. There are three types of molybdenum–molybdenum bonds; two of these, denoted d_1 and d_2, are intracluster, while one, denoted d_3, is intercluster. The intracluster d_1 and d_2 bonds are approximately parallel and perpendicular to the c-axis respectively. The cavities which exist between the Mo_6X_8 units are interconnected and accommodate the ternary metal element in the Chevrel phase compounds of composition $M_xMo_6X_8$. Structural studies of the closely related molybdenum–metal chalcogenides $Mo_{4.5}Ru_{1.5}Te_8$, $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$ have confirmed (4, 6) the partial substitution of molybdenum by ruthenium and rhenium in the metal cluster.

Bonding in the Chevrel phases has been described in terms of the ionic–covalent model (1, 7). The basic tenet of this model is that 12 covalent Mo–Mo bonds exist in

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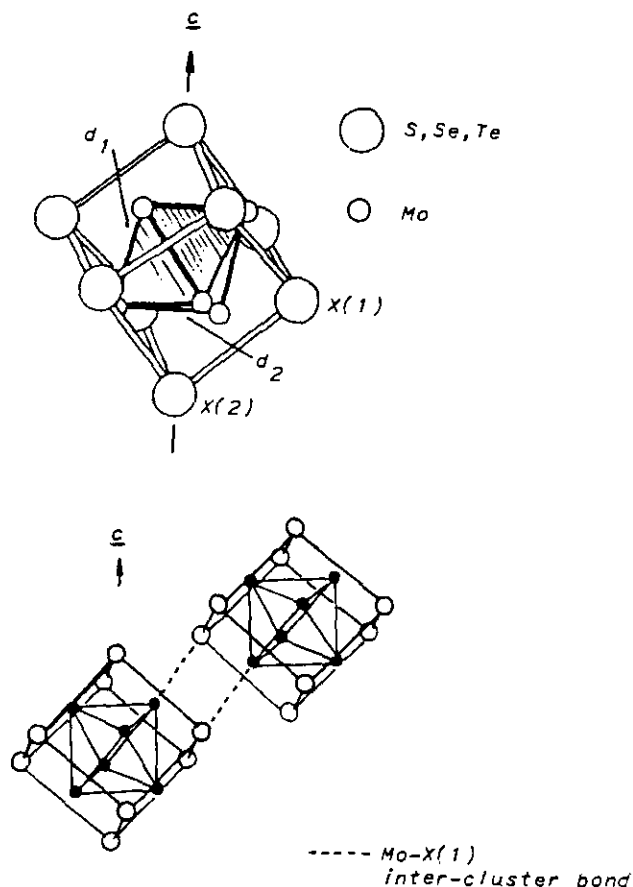
FIG. 1. The Mo_6X_8 (X = S, Se, Te) unit showing the $X(1)$ and $X(2)$ chalcogen sites and the d_1 and d_2 molybdenum–molybdenum bonds (above). Two Mo_6X_8 units of the compounds Mo_6X_8 (X = S, Se, Te) showing the occupation of the exo position by a chalcogen from an adjacent Mo_6X_8 unit (below).

the Mo_6 cluster. While the chalcogens are considered to withdraw electrons, the ternary element donates valence electrons to the Mo_6 cluster. The additional electrons introduced by the ternary metal can be visualized as reducing the Mo_6 cluster. For example, the Mo_6 cluster in $SnMo_6S_8$ can be initially associated with 36 electrons derived from the six valence electrons of each molybdenum atom. Sixteen electrons can be envisaged as being withdrawn from the cluster by each divalent sulfur, while the adoption by tin of a +2 oxidation state finally results in 22 electrons being associated with the Mo_6 cluster.

A characteristic feature of bonding in all the Chevrel phase sulfides and selenides (1, 7), and the closely related $Mo_{6-x}M_xSe_8$-type compounds (6), is that the introduction of additional electrons into the structure results in a reduction in the intracluster metal separations (Table 1). This effect, which has been called the electronic effect, has been attributed (1, 6, 7) to the occupation of intracluster bonding orbitals by the additional electrons.

The nature of bonding in the Chevrel phase compounds was reassessed (9) in 1981 and many of the structural features were associated with strong Mo–X(1) intercluster bonds (see Fig. 1). It was noted that a characteristic feature of Mo_6Y_8 (Y = chalcogenide, halide) cluster chemistry is that the exo position of the cluster is strongly bonded to some basic group; e.g., pyridine in Mo_6S_2-$Cl_2.6Py$ and chloride ions in Mo_6Cl_{12}. This exo position lies adjacent to the molybdenum atom in each face of the cluster. The molybdenum atoms were therefore envisaged as showing a Lewis acid character (9). It was shown that Mo–Mo bonding is not inhibited in Mo_6Y_8-type compounds in which ligands additional to the Mo_6Y_8 unit occupy the exo positions. In contrast, the binary compounds Mo_6X_8 (X = S, Se, Te) have no additional ligands to occupy the exo positions. In these compounds the $X(1)$ atoms from neighboring Mo_6X_8 units occupy the exo positions (Fig. 3), satisfying the requirement that these sites be filled. These intercluster Mo–X(1) bonds are so strong that the clusters and the Mo–Mo intracluster bonds are elongated along the c axis and Mo–Mo bonding is inhibited.

No detailed description of the nature of the bonding in tellurium analogues of these types of compounds has yet been reported.

DISCUSSION

Bonding in $Mo_{4.5}Ru_{1.5}Te_8$ and $Ni_{0.85}Mo_6Te_8$

The introduction of ruthenium, and hence additional electrons, into the metal cluster in $Mo_{4.5}Ru_{1.5}Te_8$ shortens the metal–Te(1) intercluster distance and slightly lengthens intracluster metal–metal separations as compared to those in Mo_6Te_8 (Table 1 and Fig. 2). The standard deviation for all distances is of the order of 0.005 Å. In distinct contrast the corresponding distances in the Chevrel phase compounds and mixed metal selenides such as $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$ increase and decrease respectively as additional electrons are introduced into the structure. This is well illustrated in Fig. 2 which shows that whilst the introduction of up to three additional electrons has no effect on the average intracluster metal separations in the tellurides, the introduction of a similar number of additional electrons in the sulfides and selenides reduces the same distance by ca. 0.1 Å. Hence, the intracluster metal separations show that the electronic effect does not occur in $Mo_{4.5}Ru_{1.5}Te_8$. This sharply contrasts with all previous descriptions of bonding in the Chevrel phase sulfides, selenides, and the compounds $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$. A consideration of the interatomic distances in $Ni_{0.85}Mo_6Te_8$ indicates that the electronic effect is also absent in this compound (Table 1, Fig. 2).

The absence of the electronic effect in the telluriumcontaining compounds may be a result of the band struc-

TABLE 1

Interatomic Distances for Selected Chevrel and Related Phases

Compound	Metal–metal intracluster distances (Å)		Metal–metal intercluster distance (Å)	Cluster metal–$X(1)$ intercluster distance (Å)	References
	d_1 (×2)	d_2 (×2)	d_3		
Mo_6S_8	2.862	2.698	3.084	2.425	(1)
$Cu_{1.8}Mo_6S_8$	2.752	2.683	3.237	2.494	(1)
$Cu_{2.76}Mo_6S_8$	2.708	2.671	3.330	2.527	(1)
$Cu_{2.94}Mo_6S_8$	2.697	2.665	3.353	2.541	(1)
$Cu_{3.66}Mo_6S_8$	2.681	2.659	3.389	2.551	(1)
$LaMo_6S_8$	2.707	2.667	3.238	2.590	(8)
$SnMo_6S_8$	2.737	2.688	3.232	2.550	(8)
$AgMo_6S_8$	2.804	2.706	3.154	2.459	(8)
Mo_6Se_8	2.836	2.684	3.266	2.599	(6)
$PbMo_6Se_8$	2.734	2.697	3.490	2.722	(8)
$Cu_{1.0}Mo_6Se_8$	2.771	2.691	3.363	2.632	(1)
$Cu_{1.5}Mo_6Se_8$	2.752	2.685	3.412	2.643	(1)
$Cu_{2.0}Mo_6Se_8$	2.727	2.680	3.491	2.673	(1)
$La_{0.8}Mo_6Se_8$	2.725	2.682	3.446	2.730	(8)
$Sn_{0.8}Mo_6Se_8$	2.755	2.680	3.419	2.694	(8)
$AgMo_6Se_8$	2.776	2.701	3.378	2.640	(8)
$Mo_4Ru_2Se_8$	2.710	2.659	3.386	2.623	(6)
$Mo_{1.5}Re_{4.5}Se_8$	2.672	2.632	3.406	2.635	(6)
Mo_6Te_8	2.772	2.700	3.674	2.837	(1)
$M_{4.5}Ru_{1.5}Te_8$	2.779	2.718	3.713	2.782	(4)
$Ni_{0.85}Mo_6Te_8{}^a$		2.739	3.678	2.833	(5)

^{a} Average distances.

ture of these materials and the relative energies of the chalcogen valence p orbitals. The band structure of compounds of the type $Mo_{6-x}Ru_xSe_8$ has been deduced from photoelectron spectroscopy (10) and band structure calculations (11) (Fig. 3). The position of the Fermi level lies in the Mo, Ru $4d$ cluster bonding band or the cluster- and metal–chalcogen antibonding bands, depending on the degree of substitution of molybdenum by ruthenium. Figure 3 shows that the selenium $4p$ nonbonding band lies well below both the Fermi level and the Mo, Ru $4d$ cluster bonding band. However, tellurium $5p$ orbitals are higher in energy than selenium $4p$ orbitals. Calculations (11) suggest that the tellurium $5p$ nonbonding band overlaps with the Mo, Ru $4d$ cluster bonding band. This may result in the filling of the Mo, Ru $4d$ cluster bonding band by electrons from the tellurium $5p$ electrons. Thus in Mo_6Te_8 the cluster bonding band is likely to be full, and additional electrons resulting from the substitution of molybdenum by ruthenium will occupy the tellurium $5p$ nonbonding band. No shortening of metal–metal intracluster separations would therefore be expected according to such a model and none is observed. In contrast, additional electrons in the corresponding sulfides and selenides resulting from the substitution of molybdenum by ruthenium oc-

cupy the $4d$ cluster bonding band, resulting in shorter metal–metal intracluster separations. It has been pointed out that the charge on tellurium is less than that on selenium or sulfur. The chemical nature of tellurium, and whether it is best envisaged as Te^- or Te^{2-}, remain to be established. The discussions in this paper are valid irrespective of the charge attributed to tellurium.

It is now necessary to consider the effects of increasing the number of electrons in the metal cluster on the metal–$X(1)$ intercluster distances. The introduction of additional electrons into the metal cluster of the Chevrel phase sulfides, selenides, and $Mo_{6-x}M_xSe_8$-type compounds is accompanied by a steady increase in the cluster metal–$X(1)$ intercluster distance (Table 1). This is shown for the selenides in Fig. 4. In contrast, the introduction of electrons into the metal cluster of Mo_6Te_8 by the substitution of molybdenum by ruthenium causes a decrease in the corresponding distance (Table 1). The anomalous behaviour of $Mo_{4.5}Ru_{1.5}Te_8$ can be understood if the ruthenium atoms enhance the Lewis acidity of the cluster-metal sites in this compound to a greater extent than in Mo_6Te_8. The random occupation of ruthenium atoms within the metal cluster (4) may be considered to cause an increase in the average Lewis acidity of the metal sites which
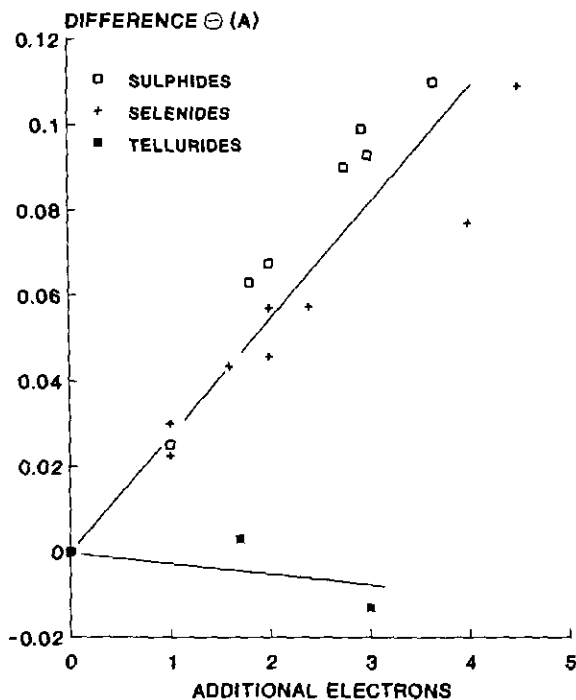
FIG. 2. Difference θ between average metal–metal intracluster separations in compounds of the type $M_x Mo_6 X_8$ and $Mo_{6-x} M_x X_8$ ($X = $ S, Se, Te) and the corresponding distance in the binary compounds $Mo_6 X_8$ ($X = $ S, Se, Te).

FIG. 4. Cluster metal–Se(1) intercluster distances for the Chevrel phase selenides and for $Mo_4 Ru_2 Se_8$ and $Mo_{1.5} Re_{4.5} Se_8$.

leads, as observed, to a shortening of the metal–Te(1) intercluster distance which contributes to the lengthening of the intracluster metal–metal bonds (Table 1, Fig. 2).

To understand why the Lewis acidity of the metal sites is increased by the incorporation of ruthenium, the electronic environments and oxidation states of the metal
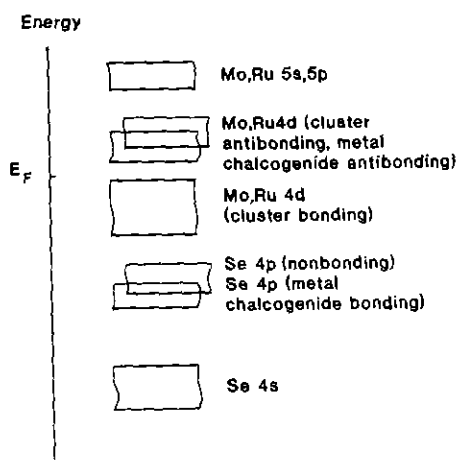

FIG. 3. Band structure for compounds of the type $Mo_{6-x} Ru_x Se_8$, as deduced from photoelectron spectroscopy (10) and band structure calculations.
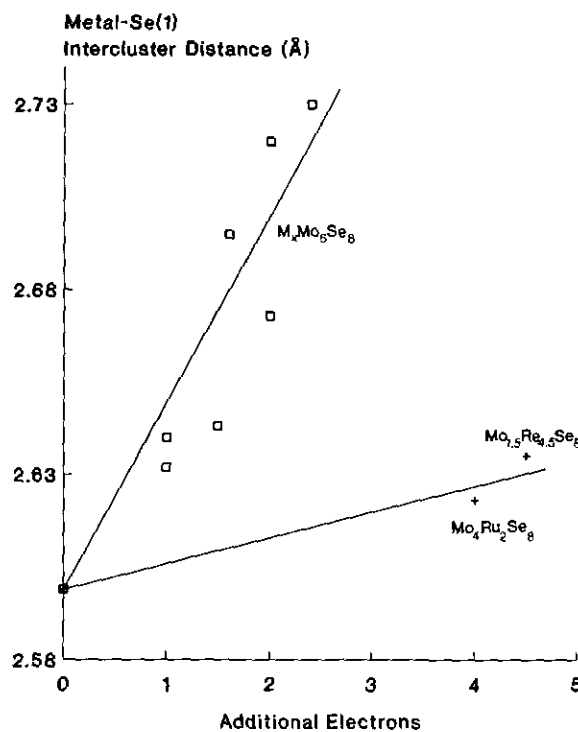
atoms must be considered. Although these compounds are best described by a mixture of ionic and covalent bonding, their representation in terms of ionic formulae enables the polarizing ability of the metal atoms in the cluster to be assessed. If tellurium is assumed to be present as Te^{2-}, then subtraction of the 8×2 electrons required by the tellurium atoms from the 36 metal valence electrons in $Mo_6 Te_8$ leaves 20 electrons in the Mo_6 cluster. Each molybdenum atom can therefore be associated with 3.33 electrons and an oxidation state of $2.67+$, and $Mo_6 Te_8$ can be represented by the formula $Mo_6^{2.67+} Te_8^{2-}$.

For $Mo_{4.5} Ru_{1.5} Te_8$ there are 39 metal valence electrons; hence, subtraction of the 16 electrons required by the tellurium atoms results in 23 electrons being associated with the metal cluster. By assuming that the electrons involved in metal–metal bonding are delocalized over the cluster, each metal atom can be considered as having the same electronic environment. The molybdenum and ruthenium atoms in $Mo_{4.5} Ru_{1.5} Te_8$ can therefore each be associated with 3.83 electrons and with oxidation states of $2.17+$ and $4.17+$ respectively. The compound $Mo_{4.5} Ru_{1.5} Te_8$ can therefore be represented by the formula $Mo_{4.5}^{2.17+} Ru_{1.5}^{4.17+} Te_8^{2-}$.

Hence, we suggest that the high oxidation state of the ruthenium atom in the cluster results in an increase in the Lewis acidity of the metal sites and to the polarization of the tellurium $5p$ electrons and a consequent shortening

of the average cluster metal–Te(1) intercluster distance. Similar effects might also be expected in the closely related selenides $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$ and this is discussed in the next section.

Finally, it is worth commenting that nickel in $Ni_{0.85}Mo_6Te_8$ would be expected to introduce additional electrons into the structure, so that the oxidation state and Lewis acidity of the molybdenum atoms would diminish and the average Mo–Te(1) intercluster distance would be expected to be longer than that observed in Mo_6Te_8. However, the data in Table 1 show that these distances are very similar. We suggest that the distance is prevented from increasing in $Ni_{0.85}Mo_6Te_8$ by strong Mo–Ni bonds, as indicated by the short (2.603 Å) interatomic distances (5). In this respect it is interesting to note that strong Mo–Ni bonds have also been identified (9) in the nickel-containing Chevrel phase sulfides and selenides $(Ni_xMo_6X_8, X = S, Se)$.

New Observations for $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$

The mixed metal selenides $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$ have been the subject of an earlier study (6) in which interatomic distances were reported, bonding properties discussed, and the occurrence of the electronic effect in these compounds identified. The introduction of additional electrons into the metal cluster can be seen to increase the metal–Se(1) intercluster distances and to decrease the metal–metal intracluster separations in a manner similar to that observed in the Chevrel phase compounds (Table 1).

Effects similar to those observed in $Mo_{4.5}Ru_{1.5}Te_8$ might also be expected to occur in $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$. For example, the incorporation of ruthenium or rhenium into the cluster might be expected to increase the Lewis acidity of the metal sites. This would be expected to lead to a shortening of the metal–Se(1) intercluster separations. A detailed comparison of this distance is achieved by an examination of Fig. 4, which depicts the variation of cluster metal–Se(1) distances as a function of additional electrons. The results show that the cluster metal–Se(1) intercluster distance in $Mo_4Ru_2Se_8$ and $Mo_{1.5}Ru_{4.5}Se_8$ increases more slowly on reduction of the host structure than in the Chevrel phase selenides $M_xMo_6Se_8$. It would appear therefore that the reduction of the cluster metal–Se(1) intercluster distances in $Mo_4Ru_2Se_8$ and $Mo_{1.5}Re_{4.5}Se_8$ is diminished by the increasing acidity of the metal sites. Hence it seems that in the mixed metal selenides the electronic effect is dominant and coexists with an increased acidity of the metal sites resulting from the incorporation of ruthenium or rhenium.

Cluster Metal–X (X = S, Se, Te)
Intracluster Separations

In a previous section the effect of changes in cluster metal oxidation state and Lewis acidity on intercluster

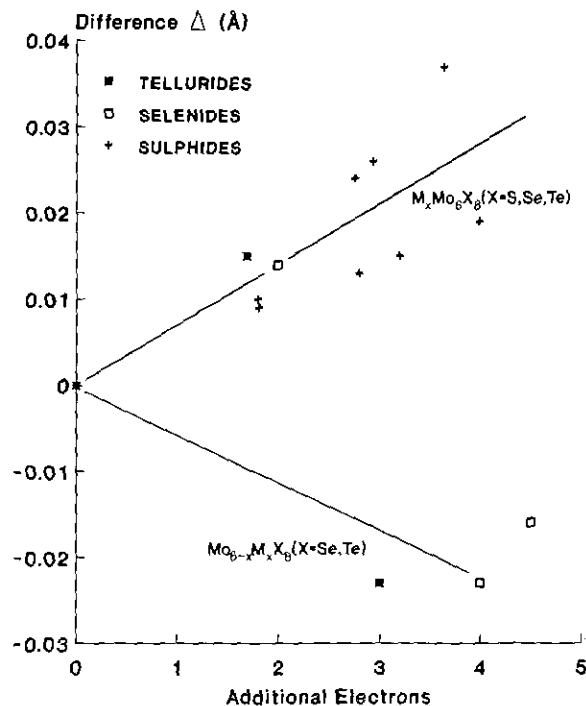FIG. 5. Difference Δ between average M–X (M = metal-cluster atom Mo, Ru, Re; X = S, Se, Te) intracluster separation in Chevrel phase compounds and molybdenum metal chalcogenides, and the corresponding distance in the binary compounds Mo_6X_8 (X = S, Se, Te).

metal–X(1) distances were described. It is therefore appropriate to consider whether cluster metal–X intracluster separations might behave in a similar fashion. Average cluster metal–X intracluster distances were therefore calculated from published data and plotted as a function of additional electrons (Fig. 5 and Table 2). The results show that for compounds of the type $M_xMo_6X_8$ (X = S, Se, Te), the decrease in oxidation state of the molybdenum atoms resulting from the introduction of additional electrons causes an increase in the average Mo–X intracluster separation. In contrast, the molybdenum metal chalcogenides $Mo_{6-x}M'_xX_8$ (M' = Ru, Re; X = Se, Te) have shorter average cluster metal–X intracluster separations as compared to the binary compounds Mo_6Se_8 and Mo_6Te_8 and we associate this with the polarization of the chalcogen valence p orbitals by the ruthenium or rhenium (vide infra). It appears that the correlation that exists between cluster metal–X(1) intercluster separations, the metal oxidation state, and the Lewis acidity of the cluster metal sites also exists for cluster metal–X intracluster separations. These results demonstrate that cluster metal oxidation states influence both intra- and intercluster metal–chalcogen separations in a systematic and predictable fashion.

The ^{125}Te Mössbauer spectra recorded from the compounds $Mo_{6-x}M'_xTe_8$ (M' = Ru, Rh) give further evidence

TABLE 2

Average Metal–X Intracluster Separations for some Chevrel and Related Phases, and the Difference from the Same Separation in the Corresponding Binary Compound Mo_6X_8 (X = S, Se, Te)

Compound	Average metal–X intracluster separation (Å)	Difference Δ from the corresponding binary compound (Å)	Number of additional electrons associated with cluster	Reference
Mo_6Te_8	2.752	0	0	(8)
$Mo_{4.5}Ru_{1.5}Te_8$	2.729	−0.023	3	(4)
$Ni_{0.85}Mo_6Te_8$	2.767	0.015	1.7	(5)
Mo_6Se_8	2.563	0	0	(6)
$Mo_4Ru_2Se_8$	2.540	−0.023	4	(6)
$Mo_{1.5}Re_{4.5}Se_8$	2.547	−0.016	4.5	(6)
$PbMo_6Se_8$	2.577	0.014	2	(12)
Mo_6S_8	2.439	0	0	(8)
$Cu_{1.8}Mo_6S_8$	2.449	0.010	1.8	(8)
$Cu_{2.76}Mo_6S_8$	2.463	0.024	2.76	(8)
$Cu_{2.94}Mo_6S_8$	2.465	0.026	2.94	(8)
$Cu_{3.66}Mo_6S_8$	2.476	0.037	3.66	(8)
$Ni_{1.4}Mo_6S_8$	2.452	0.013	2.8	(13)
$Ni_2Mo_6S_8$	2.458	0.019	4	(14)
$Co_{1.6}Mo_6S_8$	2.454	0.015	3.2	(13)
$Fe_{1.32}Mo_6S_8$	2.457	0.018	2.64	(13)
$Pb_{0.92}Mo_6S_8$	2.448	0.009	1.84	(12)
$EuMo_6S_8$	2.453	0.014	2	(15)
$SrMo_6S_8$	2.452	0.013	2	(15)
$BaMo_6S_8$	2.454	0.015	2	(15)
$CaMo_6S_8$	2.452	0.013	2	(16)

for the polarization of tellurium $5p$ electrons by the substitution of ruthenium and rhodium into the molybdenum cluster. The ^{125}Te Mössbauer parameters of these compounds are presented in Table 3. Both the chemical isomer shift and the linewidth data increase with increasing ruthenium concentration in these compounds (Fig. 6). Since the tellurium is anionic and the $5s$ and $5p$ orbitals contain between six and eight electrons, the absence of resolved quadrupole splitting suggests a similar distribution of electrons in the $5p$ orbitals. The increase in linewidth with

TABLE 3

^{125}Te Mössbauer Parameters Recorded from Compounds of the Type $Mo_{6-x}M_xTe_8$ (M = Ru, Rh)

Compound	$\delta \pm 0.15$ mm/s[a]	$\Gamma \pm 0.2$ mm/s
Mo_6Te_8	0.41	7.00
$Mo_{5.5}Ru_{0.5}Te_8$	0.42	7.12
$Mo_5Ru_1Te_8$	0.48	7.30
$Mo_{4.5}Ru_{1.5}Te_8$	0.47	7.62
$Mo_{5.5}Rh_{0.5}Te_8$	0.50	7.85

[a] Relative to ^{125}Sb/Rh source.

increasing ruthenium content in the metal cluster may be associated with the increasing unresolved quadrupole splitting, and therefore an increasing imbalance in the number of electrons in the tellurium $5p$ orbitals. This may be associated with electron drift or polarization of the tellurium $5p$ electrons towards the $Mo_{6-x}Ru_x$ cluster. This interpretation is supported by the observed increase in the ^{125}Te Mössbauer chemical isomer shift data which accompanies the increase in ruthenium content of the metal cluster and which is indicative of the deshielding of the tellurium $5s$ electron density at the nucleus as a result of the removal of $5p$ electrons.

The validity of this proposal is supported by consideration of the ^{125}Te Mössbauer linewidth and isomer shift data for $Mo_{5.5}Rh_{0.5}Te_8$ and $Mo_{5.5}Ru_{0.5}Te_8$. The larger values of δ and Γ for $Mo_{5.5}Rh_{0.5}Te_8$ are consistent with the ionic formulae of these compounds ($Mo_{5.5}^{2.42+}Rh_{0.5}^{5.42+}Te_8^{2-}$ and $Mo_{5.5}^{2.5+}Ru_{0.5}^{4.5+}Te_8^{2-}$), which suggests that the polarization of tellurium $5p$ electrons will be greatest in the rhodium-containing material (Table 3). Thus the ^{125}Te Mössbauer spectra recorded from $Mo_{6-x}M_xTe_8$ (M = Ru, Rh) provide further evidence for the polarization of tellurium $5p$ electrons by ruthenium or rhodium substitution into the molybdenum cluster.
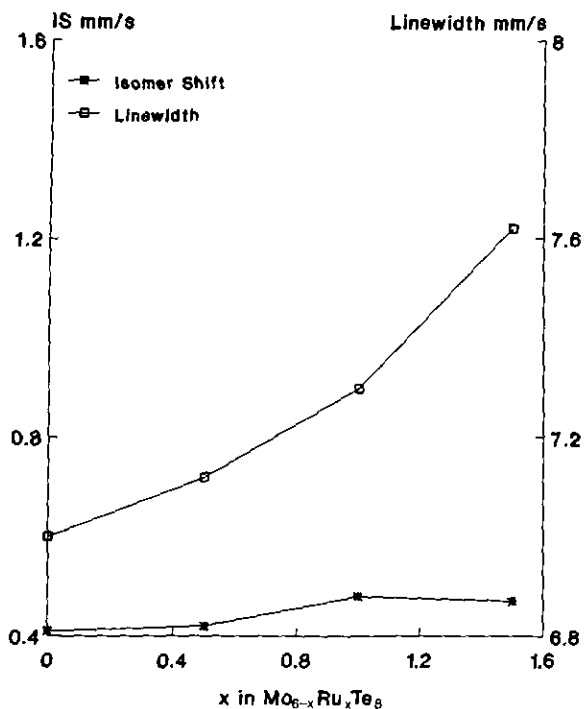
FIG. 6. Variation of [125]Te Mössbauer chemical isomer shifts and spectral linewidths with ruthenium content in compounds of the type $Mo_{6-x}Ru_xTe_8$.

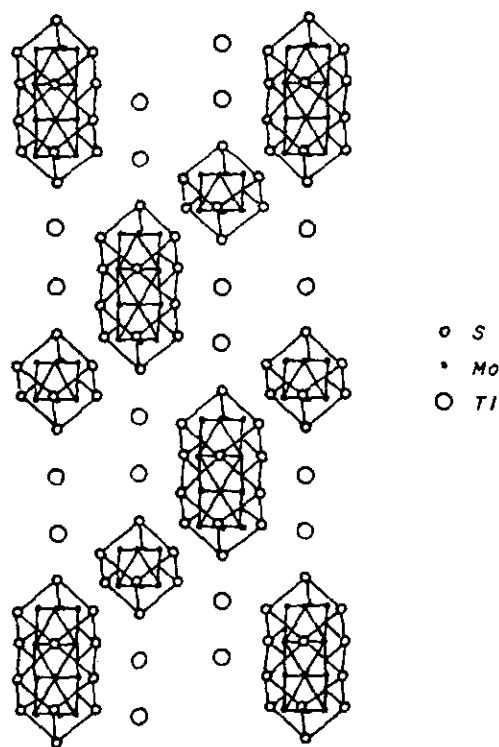## Compounds Containing Condensed Mo_6X_8 Clusters of the Type $Mo_{3n}X_{3n+2}$

A number of materials related to the Chevrel phase compounds which contain clusters consisting of more than six molybdenum atoms have been reported (8). These clusters may be visualized as resulting from condensation of Mo_6X_8 units. For example, the compound $Tl_2Mo_9S_{11}$ contains $Mo_{12}S_{14}$ units which may be envisaged as resulting from the condensation of three Mo_6S_8 units (see Fig. 7). Since these compounds are closely related to the Chevrel phase compounds a similar relationship between intracluster Mo–X distances and oxidation state, and therefore Lewis acidity of the cluster metal atoms, might be expected. Average Mo–X intracluster separations were therefore calculated from available interatomic distances and plotted as a function of average oxidation state of the molybdenum atom (see Table 4 and Fig. 8). The results show that $Mo_{3n}X_{3n+2}$-type clusters behave in a similar fashion to $Mo_6X_8^-$ and $Mo_{6-x}M_xX_8$-type clusters in that increasing oxidation state and Lewis acidity of the cluster metal atom are correlated with decreasing cluster metal–X intracluster separations.

FIG. 7. The structure of $Tl_2Mo_9S_{11}$ showing the Mo_6S_8 and $Mo_{12}S_{14}$ units.

TABLE 4

Average Values of Oxidation State of Molybdenum Atoms and Mo–X Intracluster Distance for Compounds of the Type $M_xMo_{3n}X_{3n+2}$

Compound	Average oxidation state of molybdenum	Average Mo–X intracluster separation (Å)	Reference
Mo_6S_8	2.67	2.439	(8)
$BaMo_6S_8$	2.33	2.454	(15)
$Tl_2Mo_9S_{11}$	2.22	2.478	(17)
$K_2Mo_6S_6$	1.67	2.503	(18)
$Rb_2Mo_6S_6$	1.67	2.545	(18)
$Cs_2Mo_6S_6$	1.67	2.583	(18)
Mo_6Se_8	2.67	2.563	(6)
$In_2Mo_{15}Se_{19}$	2.40	2.591	(8)
$In_{2.9}Mo_{15}Se_{19}$	2.34	2.591	(8)
$In_{3.33}Mo_{15}Se_{19}$	2.31	2.591	(8)
$Li_{3.2}Mo_6Se_8$	2.13	2.593	(19)
$Rb_4Mo_{18}Se_{20}$	2.00	2.630	(20)
$Tl_2Mo_6Se_6$	1.67	2.666	(21)
$Tl_2Mo_6Se_6$	1.67	2.648	(22)
$In_2Mo_6Se_6$	1.67	2.650	(22)
Mo_6Te_8	2.67	2.752	(1)
$Ni_{0.85}Mo_6Te_8$	2.38	2.767	(5)
$AgMo_6Te_6$	1.83	2.843	(23)
$In_2Mo_6Te_6$	1.67	2.793	(22)
$Tl_2Mo_6Te_6$	1.67	2.815	(22)

Note. Sulfur, selenium, and tellurium are assigned oxidation states of −2.
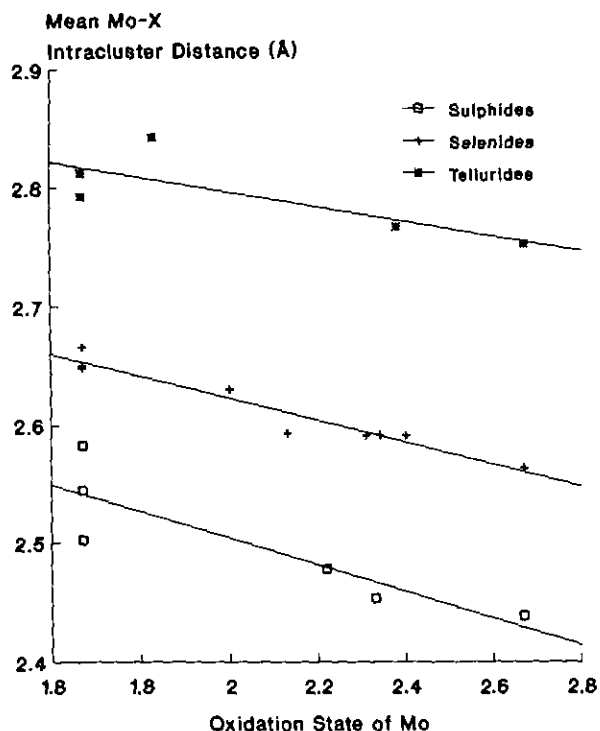
Mean Mo-X
Intracluster Distance (Å)

FIG. 8. Variation in average Mo-X (X = S, Se, Te) intracluster distances with average oxidation state of molybdenum for compounds of the type $M_xMo_{3n}X_{3n+2}$.

CONCLUSIONS

Bonding in tellurium analogues of the Chevrel phase compounds has been compared to that in the closely related sulfides and selenides. A major difference is that while the sulfides and selenides exhibit the electronic effect, or increased metal intracluster bonding due to the introduction of additional electrons into the cluster, the tellurides do not. This has been interpreted in terms of the band structures of these compounds and the relative energies of the chalcogen valence p orbitals.

The oxidation states of metal atoms in the metal cluster, which are related to the number of additional electrons introduced into the metal cluster and the substitution of molybdenum by ruthenium, rhenium, or rhodium, have been shown to influence cluster metal-X(1) intercluster

and cluster metal-chalcogen intracluster separations. This has been associated with the polarization of the chalogen valence p orbitals by the Group VIII metal in the cluster.

REFERENCES

1. K. Yvon, in "Current Topics in Materials Science" (E. Kaldis, Ed.), Vol. 3, p. 53. North-Holland, Amsterdam, 1979.
2. F. J. Berry and C. D. Gibbs, *J. Chem. Soc. Dalton Trans.*, 57. (1991).
3. F. J. Berry and C. D. Gibbs, *Hyperfine Interactions* 66, 367 (1991).
4. F. J. Berry, C. D. Gibbs, and C. Greaves, *J. Solid State Chem.* 92, 148 (1991).
5. W. Hönle and K. Yvon, *J. Solid State Chem.* 70, 235 (1987).
6. H. D. Flack, W. Hönle, and K. Yvon, *J. Solid State Chem.* 49, 157 (1983).
7. A. Paoli and K. Yvon, *Solid State Commun.* 24, 41 (1977).
8. R. Chevrel and M. Sergent, in "Superconductivity in Ternary Compounds" (Ø. Fischer and M. B. Maple, Eds.), Vol. 1, p. 25. Springer-Verlag, Berlin/Heidelberg, 1982.
9. J. D. Corbett, *J. Solid State Chem.* 39, 56 (1981).
10. N. Vante, W. Jaegermann, H. Tributsch, W. Hönle, and K. Yvon, *J. Am. Chem. Soc.* 109, 3251 (1987).
11. H. Nohl, W. Klose, and O. K. Andersen, in "Superconductivity in Ternary Compounds" (Ø. Fischer and M. B. Maple, Eds.), Vol. 1, p. 165. Springer-Verlag, Berlin/Heidelberg, 1982.
12. J. Guillevic, H. Lestrat, and D. Grandjean, *Acta Crystallogr. Sect. B* 32, 1342 (1976).
13. J. Guilleric, O. Bars, and D. Grandjean, *Acta Crystallogr. Sect. B* 32, 1338 (1976).
14. O. Bars, D. Grandjean, and J. Guillevic, *J. Solid State Chem.* 7, 158 (1973).
15. K. Kubel and K. Yvon, *Acta Crystallogr. Sect. C* 43, 1655 (1987).
16. F. Kubel and K. Yvon, *J. Solid State Chem.* 73, 188 (1988).
17. M. Potel, R. Chevrel, and M. Sergent, *Acta Crystallogr. Sect. B* 36, 1319 (1980).
18. J. Huster, G. Schippers, and W. Bronger, *J. Less-Common Met.* 91, 333 (1983).
19. R. J. Cava, A. Santoro, and J. M. Tarascon, *J. Solid State Chem.* 54, 193 (1984).
20. P. Gougeon, M. Potel, J. Padiou, and M. Sergent, *Mater. Res. Bull.* 23, 453 (1988).
21. M. Potel, R. Chevrel, and M. Sergent, *Acta Crystallogr. Sect. B.* 36, 1545 (1980).
22. W. Hönle, H. G. von Schnering, A. Lipka, and K. Yvon, *J. Less-Common Met.* 71, 135 (1980).
23. P. Gougeon, M. Potel, J. Padiou, and M. Sergent, *J. Solid State Chem.* 68, 137 (1987).