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Matrix Effect in Chevrel Phases Containing Divalent Metal Cations. The Structure of Rhombohedral $CaMo_6S_8$

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The structure of $CaMo_6S_8$ was refined from single crystal X-ray data at 298 K (space group $R\bar{3}$, a = 6.5146(5) Å, α = 89.63(1)°, R = 0.032 for 720 reflections with $I > 3\sigma(I)$ and 25 parameters). Comparison with isoelectronic MMo_6S_8 ($M = Yb^{2+}, Eu^{2+}, Sr^{2+}, Ba^{2+}$) confirms the matrix effect predicted by J. D. Corbett (*J. Solid State Chem.* **39,** 56 (1981)). As the cell volume increases across this series the Mo_6 cluster contracts along its ternary axes by 0.021(1) Å. The strengthening of the Mo–Mo *intra*cluster bonds correlates with a weakening of the Mo–Mo and Mo–S *inter*cluster bonds.

Introduction

The elongation of the octahedral Mo_6 cluster along its ternary axis in rhombohedral Chevrel phases MMo_6X_8 (M = metal, X = chalcogen) was rationalized in terms of both electronic and geometrical factors. The electronic factor was found to originate from partially filled, overlapping energy bands (*1*) and to lead to a decrease of the cluster elongation by a gradual filling of Mo–Mo bonding states due to charge transfer (*2*). The correlation between charge transfer as expressed by the cluster-valence electron concentration (VEC) and the cluster elongation indicated an average contraction of about 0.05 Å per transferred electron (*3*). This effect was further studied in the pseudoternary selenides $(Me_x Mo_{1-x})_6Se_8$ (Me = Ru, Re) for which the geometrical factor was assumed to be equal (*4*). The geometrical factor was investigated by Corbett (*5*) and found to originate from a combination between strong Mo–S intercluster bonds and S^{2-}–S^{2-} closed shell repulsive interactions ("matrix-effect"). According to this effect a release of repulsive S–S interactions is partly transferred to the Mo_6 cluster via the network of Mo–S intercluster bonds thus leading to a decrease of the cluster elongation. The existence of this effect was confirmed from a study of sulfides MMo_6S_8 containing divalent metal cations $M = Eu^{2+}, Sr^{2+}, Ba^{2+}$ for which contributions due to the electronic factor could be assumed to be equal (*6*). The results showed that the Mo_6 cluster elongation of the compound containing the biggest cation ($r(Ba^{2+})$ = 1.35 Å (*7*)) was smaller by about 0.01 Å than those containing the smaller cations ($r(Sr^{2+})$ = 1.18 Å, $r(Eu^{2+})$ = 1.17 Å). The purpose of the present work was to study a compound containing a relatively small cation such as

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Ca^{2+} ($r = 1.00$ Å) in order to confirm this trend and to arrive at a more quantitative estimate of the matrix effect.

Experimental and Results

A sample of nominal composition Ca Mo_6S_8 was supplied by R. Baillif. Its synthesis and physical properties were described previously (*8*). The crystal chosen for the X-ray examination had an average radius of 15 μm. All reflections could be indexed with the rhombohedral unit cell and no reflections indicating a supercell were found. Integrated intensities were collected on a CAD4 four-circle X-ray diffractometer. Cell parameters were determined by least-squares refinement of 25 measured Bragg angles in the region $28° \leq 2\theta \leq 44°$. Absorption effects were corrected by spherical absorption correction. The structure was refined by the XRAY program system (*9*) by minimizing the function $\Sigma w_i(|F_r|_i - |F_c|_i/k_i)^2$ with $w_i = 1/\sigma^2(F_r)_i$. The starting values for the atomic coordinates were those reported for $EuMo_6S_8$ (*6*) (space group $R\bar{3}$, rhombohedral setting). Convergence was considered complete when the refined parameters did not vary by more than 10^{-5}. Atomic scattering factors and anomalous dispersion factors were taken from the "International Tables for X-ray Crystallography" (*10*). The cell parameters, conditions of measurements, weights, absorption and extinction coefficients, number of parameters refined, and agreement indices at convergence are summarized in Table I. The results of the refinement are summarized in Table II. Selected interatomic distances and angles are listed in Table III. Final electron density difference maps for observed reflections showed features which did not exceed ±3e/Å^3. Refinements based on variable site occupancy factors gave no indication for the possible occurrence of defects. Diffraction experiments at low temperature confirmed a structural phase transition as suggested from measurements of physical properties (*8*).

TABLE I

EXPERIMENTAL CONDITIONS AND AGREEMENT FACTORS

Space group	$R\bar{3}$
Lattice parameters[a]	
a_{rh} [Å]:	6.5146(5)
α [°]:	89.63(1)
V_{rh} [Å^3]:	276.46(7)
a_{hex} [Å]:	9.1832(14)
c_{hex} [Å]:	11.3561(15)
V_{hex} [Å^3]:	829.38(21)
Crystal radius [mm]:	0.015
Absorption coefficient μ [mm^{-1}]:	8.31
Wavelength [Å]:	0.71069
$[\sin(\theta)/\lambda]_{max}$ [Å^{-1}]:	0.99
Scan type	$\omega - 2\theta$
Scan speed [°/min]	3.5–5.5[b]
Range of *hkl*	
h:	1 to 11
k:	−8 to 9
l:	−9 to 8
Standard reflections:	$\bar{1}\ 3\ 1$, $\bar{1}\ 1\ \bar{3}$
Max intensity variations of standard reflections:	2.9%
Internal consistency factors	
R_{int} ($R_{w,int}$):	4.5% (4.7%)
Ratio of max L.S. shift to error:	$<10^{-3}$
Number of measured (independent) reflections:	2166 (720)
Agreement indices:	
$R = \Sigma\lvert(F_0 - F_c)\rvert_i/\Sigma\lvert F_0\rvert_i$	3.2%
$R_w = (\Sigma w_i(F_0 - F_c)_i^2/\Sigma\omega_i\lvert F_0\rvert_i^2)^{1/2}$	2.4%
Goodness of fit:	0.87
Weights:	$w = 1/\sigma(F_0^2)$
Extinction coefficient ($\cdot 10^{-4}$), [°]:	0.28(1)

[a] ESD's are given in parentheses.

[b] Depending on prescan intensity: $I_{final} > 33\sigma_{I\ prescan}$ and $t < 60$ sec.

Discussion

The structural response of the $[Mo_6S_8]$ units to *M* atom substitution and in particular that of the Mo_6 clusters can be studied in Fig. 1 in which the lengths of the two Mo–Mo *intra*cluster bonds ($[Mo–Mo]_\Delta$, $[Mo_\Delta–Mo_\Delta]$), the Mo–Mo *inter*cluster bond

TABLE II

ATOMIC COORDINATES AND ANISOTROPIC THERMAL PARAMETERS[a] U_{ij} (×100, Å^2) OF $\mathrm{CaMo_6S_8}$

Space group $R\bar{3}$, rhombohedral setting.
The expression of the temperature factor is:

$$\exp[-2\pi^2\{h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}\}]$$

Ca in 1a [0, 0, 0]	
U_{11}	2.23(6)
U_{12}	−0.74(6)
$U_{\perp}$[b]	2.96
$U_{\parallel}$[b]	0.76
Mo in 6f [x, y, z; etc.]	
x	0.22568(7)
y	0.41774(7)
z	0.55977(7)
U_{11}	0.50(2)
U_{22}	0.45(2)
U_{33}	0.51(2)
U_{12}	0.00(1)
U_{13}	−0.03(1)
U_{23}	−0.04(1)
S1 in 6f [x, y, z; etc.]	
x	0.3783(2)
y	0.1269(2)
z	0.7445(2)
U_{11}	0.89(5)
U_{22}	0.54(5)
U_{33}	0.83(5)
U_{12}	−0.13(4)
U_{13}	0.07(4)
U_{23}	0.09(4)
S2 in 2c [x, x, x; etc.]	
x	0.2391(2)
U_{11}	0.89(4)
U_{12}	−0.25(3)
$U_{\perp}$[b]	1.13
$U_{\parallel}$[b]	0.40

[a] ESD's are given in parentheses.

[b] Values perpendicular and parallel to the ternary axis as obtained from the diagonalized matrix.

([Mo–Mo]$_{\text{inter}}$), and the Mo–S *inter*cluster bonds ([Mo–S]$_{\text{inter}}$) are plotted as a function of cell volume for isoelectronic $M\mathrm{Mo_6S_8}$ (M = $\mathrm{Yb^{2+}}$, $\mathrm{Ca^{2+}}$, $\mathrm{Eu^{2+}}$, $\mathrm{Sr^{2+}}$, and $\mathrm{Ba^{2+}}$). As the cell volume increases the Mo–Mo and Mo–S *inter*cluster bonds expand by up to 0.19 and 0.06 Å, respectively, whereas one of the Mo–Mo *intra*cluster bonds ([Mo$_\Delta$–Mo$_\Delta$]) contract by up to 0.02 Å. The other Mo–Mo *intra*cluster bond ([Mo–Mo]$_\Delta$) remains practically constant. Since these compounds all have the same cluster-VEC (22e$^-$ per $\mathrm{Mo_6}$ cluster) the apparent contraction of the $\mathrm{Mo_6}$ octahedron along its ternary axis as a function of cell volume can be attributed to the matrix effect postulated by Corbett (5). According to his analysis an expansion of the structure due to incorporation of larger cations M should lead to a release of $\mathrm{S^{2-}}$–$\mathrm{S^{2-}}$ closed shell repulsions which in turn should lead to a loosening of Mo–S and Mo–Mo *inter*cluster bonds and thus to a contraction of Mo–Mo *intra*cluster bonds. In the present sulfide series the magnitude of the contraction corresponds to about 0.0013 Å per Å^3 increase in cell volume. A different value

TABLE III

INTERATOMIC DISTANCES AND ANGLES[a]

Distances [Å]		
Mo–Mo	a:	2.7239(7)
	b:	2.6669(7)
	c:	3.2217(7)
Mo–S	d:	2.5103(14)
	e:	2.4523(14)
	f:	2.4470(14)
	g:	2.3989(5)
	h:	2.5629(13)
Ca–S	i:	2.7150(7)
	j:	3.0795(13)
S–S	k:	3.9192(19)
	l:	3.4398(15)
	m:	3.4921(14)
	n:	3.4244(18)
Angles [°]		
Mo–S–Mo	α:	78.84(4)
S–Mo–S	β:	101.16(4)
	γ:	88.20(5)
	δ:	170.32(5)
	ε:	92.21(4)
S–Ca–S	ζ:	72.13(3)
	η:	68.98(3)

[a] For bond labels see Fig. 2 in Ref. (6); ESD's are in parentheses.

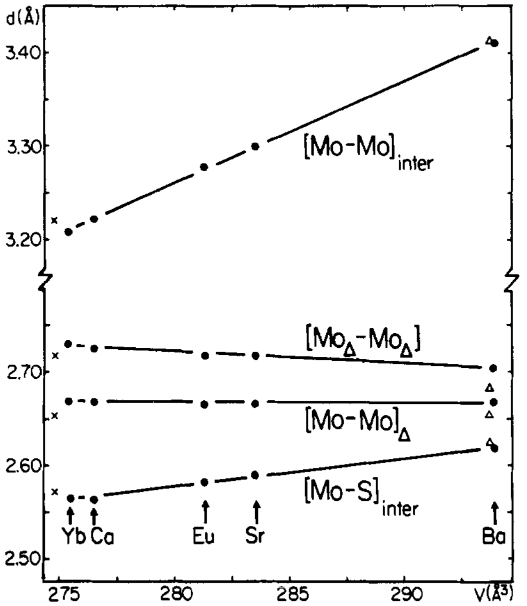

FIG. 1. *Inter*cluster [Mo–Mo] (bond label *c*), *intra*-cluster [$Mo_Δ$–$Mo_Δ$] (*a*), $[Mo–Mo]_Δ$ (*b*), and *inter*cluster [Mo–S] (*h*) distances as a function of rhombohedral cell volume. Data points for MMo_6S_8 are taken for M = Yb from Ref. (*13*) (crosses) and (*12*) (filled spots), for M = Ca from this work, for Eu, Sr, and Ba Ref. (*6*, *13*), and calculated values for Ba from Ref. (*14*) (triangles).

may be characteristic for the corresponding selenides. In the $CaMo_6S_8$ the shortest S–S distances occur between the peripheral S(1) atoms (S(1)–S(1) = 3.42 Å, bond label *n* in Fig. 2c of Ref. (*6*)) rather than between the axial and peripheral S atoms as in the other members of this series. The graphs in Fig. 1 show that the matrix effect in that compound is similar to that in the Yb compound as revealed from single crystal X-ray data (*11*). Significantly different data on the latter compound, however, were reported by high-resolution neutron powder diffraction (*12*). The latter method also yielded values for $BaMo_6S_8$ (*14*) which differed significantly from those reported (*6*) from single crystal data. The reason for these differences are not known at present. Finally the displacement amplitudes of the Ca atom perpendicular to the ternary axis ($U_\perp$ = 0.0296 Å^2) are the highest among the M atoms in the alcaline earth series ($U_\perp$ = Eu: 0.0174 Å^2 (*6*), 0.0186 Å^2 (*13*); Sr: 0.0166 Å^2 (*6*); and Ba: 0.0140 Å^2 (*6*) and are comparable to those of Yb ($U_\perp$ = 0.0272 Å^2 (*11*), 0.0342 Å^2 (*12*)). As expected from the strong M–S(2) bond parallel to the ternary axis, the displacement amplitudes of S(2) follow this trend.

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