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Thermal expansion of ternary chalcogenides of molybdenum containing infinite chains of $(Mo_{6/2}Se_{6/2})$

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The coefficients of thermal expansion of three ternary chalcogenides of molybdenum $Tl_2Mo_6Se_6$, $Cs_2Mo_6Se_6$, and $Na_2Mo_6Se_6$ have been determined in the temperature range 16 to 400° C using a Guinier–Lenne camera and a powder diffractometer. In all the three compounds, the coefficient of expansion along the c-axis ($\alpha_\parallel$) is found to be much smaller than that in the perpendicular direction ($\alpha_\perp$). This behaviour has been explained in terms of the strength of the interatomic bonds in the two directions.

1. Introduction

In 1971, Chevrel *et al.* [1] reported the existence of a new large series of ternary molybdenum chalcogenides several of which were high-field superconductors with high critical temperatures. As a sequel to these studies, a new series of compounds $M_2Mo_6X_6$ (M = Tl, Cs, Na, Rb etc., and X = chalcogen) have been prepared [2]. The structure of these compounds is mainly characterized by the presence of one-dimensional $(Mo_{6/2}X_{6/2})^1_\infty$ chains running in the direction of the hexagonal c-axis, separated by parallel chains of M atoms. The presence of these chains gives the materials a strongly anisotropic character. The resistivity of one of the compounds $Tl_2Mo_6Se_6$ perpendicular to the c-axis is found to be several hundred times larger than the resistivity parallel to the c-axis [3]. Hence, it was thought worthwhile to investigate the thermal expansion of these compounds with a view to correlating the thermal expansion with the structure and other physical properties. The present paper gives the results for three compounds $Tl_2Mo_6Se_6$, $Cs_2Mo_6Se_6$ and $Na_2Mo_6Se_6$.

2. Experimental procedure

In this investigation, a Guinier–Lenne camera supplied by Enraf–Nonius and a Siemens powder diffractometer provided with a Rigaku furnace have been used to determine the precision lattice parameters at different temperatures, as it was found that the powder samples of these substances did not give high Bragg angle reflections with a Unicam 19 cm high temperature powder camera. The samples used were kindly supplied by Dr M. Potel of the University of Rennes, France.

In the case of the Guiner-Lenne camera, precision lattice parameters in the temperature range 16 to 400° C have been determined using Cohen's [4] least squares method. The error function used is that given by Möller [5].

$$f(\theta) = -2\cot\theta/\theta\cos\alpha\cos(2\theta-\alpha) \qquad (1)$$

where θ is the Bragg angle and α is the angle between the direct beam and the normal to the plane sample. Precision lattice parameters with the powder diffractometer have been determined by the method given by le Marouille [6]. In both the cases, Cu$K\alpha$ radiation was used and the coefficients of thermal expansion at different temperatures have been evaluated using a graphical method [7]. Full experimental details of the calibration of the Guinier–Lenne camera, etc., have been described by Bencharif [8]. It may be mentioned that, though the Bragg angles of the reflections are limited to 45° in this investigation, reasonable accuracy in the measurement of the lattice parameters could be achieved on account of the higher resolution of the Guinier–Lenne camera and the powder diffractometer, compared with that of the 19 cm powder camera. One of the advantages of these instruments is that one can index the X-ray reflections unambiguously in the low Bragg angle region, especially with noncubic crystals with few space group extinctions and with large lattice parameters.

3. Results

In Table I, the lattice parameters of the three compounds obtained at room temperature in the present study are compared with the earlier data in the literature.

The study on $Na_2Mo_6Se_6$ is made only by the diffractometer method. There has been good agreement between the results obtained by the two methods for the other two compounds. Here, the results obtained by the diffractometer method only are given.

Figs 1, 2 and 3 show the variation of the lattice parameters of the three compounds at different temperatures. The temperature dependence of a and c can be represented by Equations 2 to 7, obtained by a least squares fitting of the data.

$Tl_2Mo_6Se_6$:

$$a\,(\mathrm{nm}) = 0.8930 + 0.3017\times10^{-4}T - 0.3147\times10^{-7}T^2 \qquad (2)$$

TABLE I Lattice parameters of $Tl_2Mo_6Se_6$, $Cs_2Mo_6Se_6$ and $Na_2Mo_6Se_6$ at room temperature

Source	$Tl_2Mo_6Se_6$		$Cs_2Mo_6Se_6$		$Na_2Mo_6Se_6$	
	a (nm)	*c* (nm)	*a* (nm)	*c* (nm)	*a* (nm)	*c* (nm)
Potel [10]	0.893 98(7)	0.449 37(4)	0.951	0.448	0.866	0.448
Gougeon [11]	0.894	0.450	0.954 4(3)	0.449 9(5)	0.865 5(2)	0.4485(2)
Present study:						
Guinier–Lenne camera	0.893 31(5)	0.449 06(7)	0.953 35(2)	0.448 40(5)		
Powder diffractometer	0.893 5(2)	0.450 3(5)	0.954 8(4)	0.449 7(3)	0.8656(4)	0.4486(3)

$$c\,(\text{nm}) = 0.4501 + 0.8029 + 10^{-5}T - 0.1030 \times 10^{-7}T^2 \quad (3)$$

$Cs_2Mo_6Se_6$:

$$a\,(\text{nm}) = 0.9543 + 0.2938 \times 10^{-4}T - 0.6804 \times 10^{-9}T^2 \quad (4)$$

$$c\,(\text{nm}) = 0.4496 + 0.4923 \times 10^{-5}T - 0.2670 \times 10^{-8}T^2 \quad (5)$$

$Na_2Mo_6Se_6$:

$$a\,(\text{nm}) = 0.8660 + 0.1995 \times 10^{-4}T + 0.4480 \times 10^{-8}T^2 \quad (6)$$

$$c\,(\text{nm}) = 0.4490 + 0.3510 \times 10^{-5}T - 0.2128 \times 10^{-9}T^2 \quad (7)$$

Figs 4, 5 and 6 show the variation of the coefficients of thermal expansion of the three compounds at different temperatures. The temperature dependence of the coefficients of thermal expansion $\alpha_{\parallel}$ along the *c*-axis and $\alpha_{\perp}$ at right angles to the *c*-axis are represented by Equations 8 to 13.

$Tl_2Mo_6Se_6$:

$$\alpha_{\perp} = 34.78 \times 10^{-6} - 7.05 \times 10^{-8}T \quad (8)$$

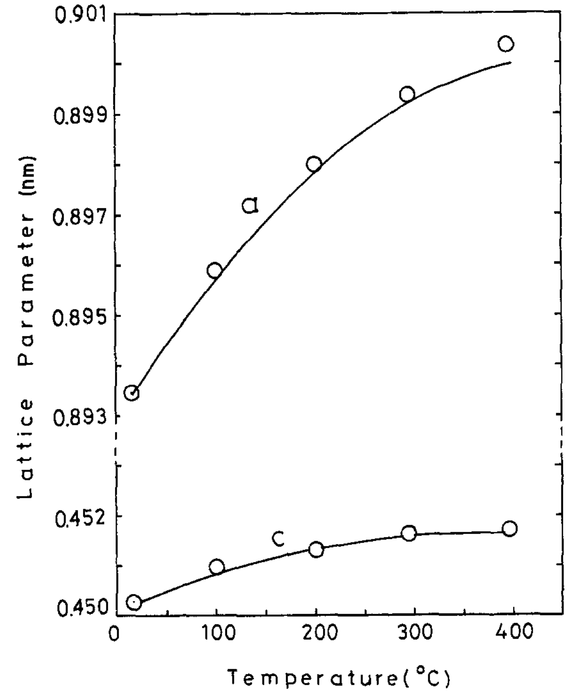

Figure 1 Variation of the lattice parameters of $Tl_2Mo_6Se_6$ with temperature.

$$\alpha_{\parallel} = 11.13 \times 10^{-6} - 1.75 \times 10^{-8}T \quad (9)$$

$Cs_2Mo_6Se_6$:

$$\alpha_{\perp} = 31.39 \times 10^{-6} - 1.42 \times 10^{-8}T \quad (10)$$

$$\alpha_{\parallel} = 10.59 \times 10^{-6} - 1.19 \times 10^{-8}T \quad (11)$$

$Na_2Mo_6Se_6$:

$$\alpha_{\leftarrow} = 23.03 \times 10^{-6} + 1.03 \times 10^{-8}T \quad (12)$$

$$\alpha_{\parallel} = 7.83 \times 10^{-6} - 9.48 \times 10^{10}T \quad (13)$$

4. Discussion

In all three compounds, the increase of the *a* and *c* parameters with temperature is non-linear. Figs 4, 5 and 6 show that in all cases, $\alpha_{\perp}$ is much greater than $\alpha_{\parallel}$, exhibiting a large anisotropy in thermal expansion. In all cases except for $Na_2Mo_6Se_6$, the coefficients of thermal expansion decrease with increasing temperature, which is not quite normal. One would expect that

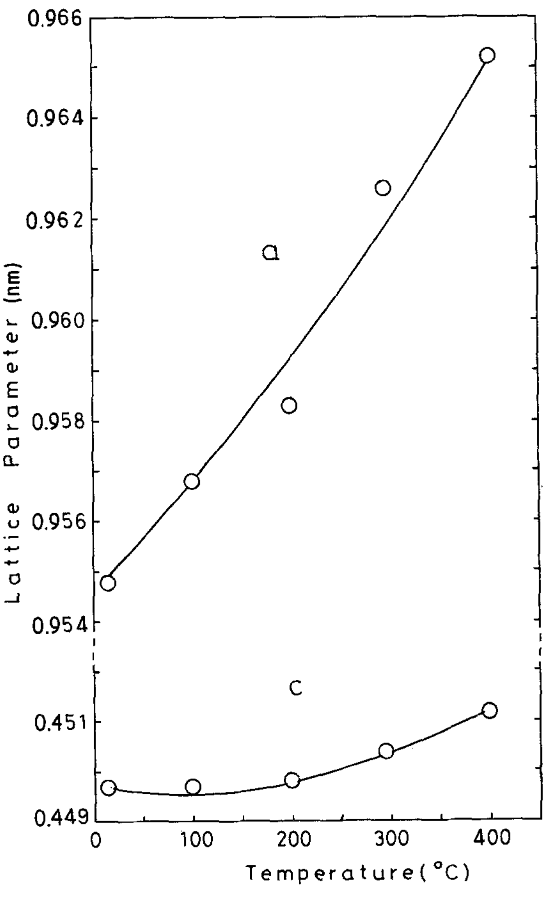

Figure 2 Variation of the lattice parameters of $Cs_2Mo_6Se_6$ with temperature.

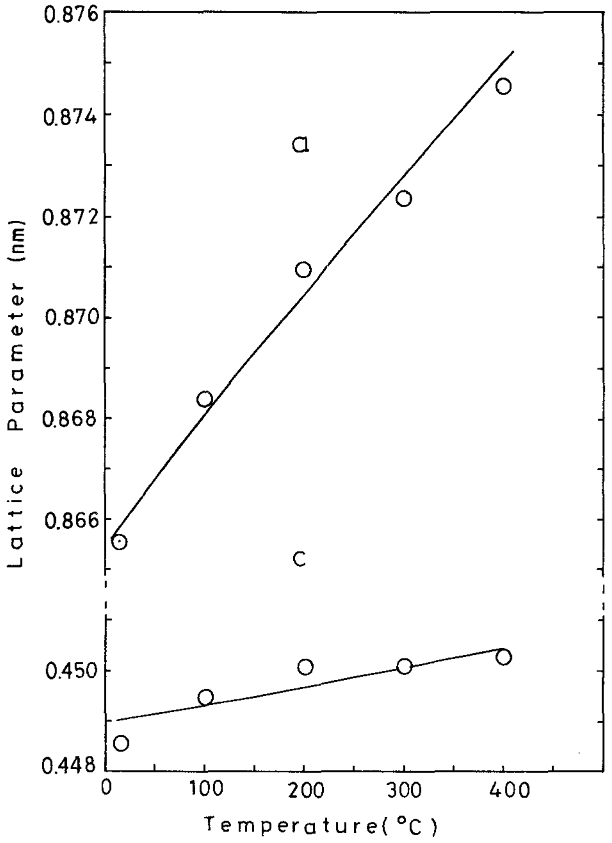

Figure 3 Variation of the lattice parameters of $Na_2Mo_6Se_6$ with temperature.

the coefficients of thermal expansion increase with increasing temperature. However, similar instances are found in the literature [9]. In what follows, an attempt is made to explain the anisotropy of thermal expansion in terms of the crystal structure and the inter atomic distances.

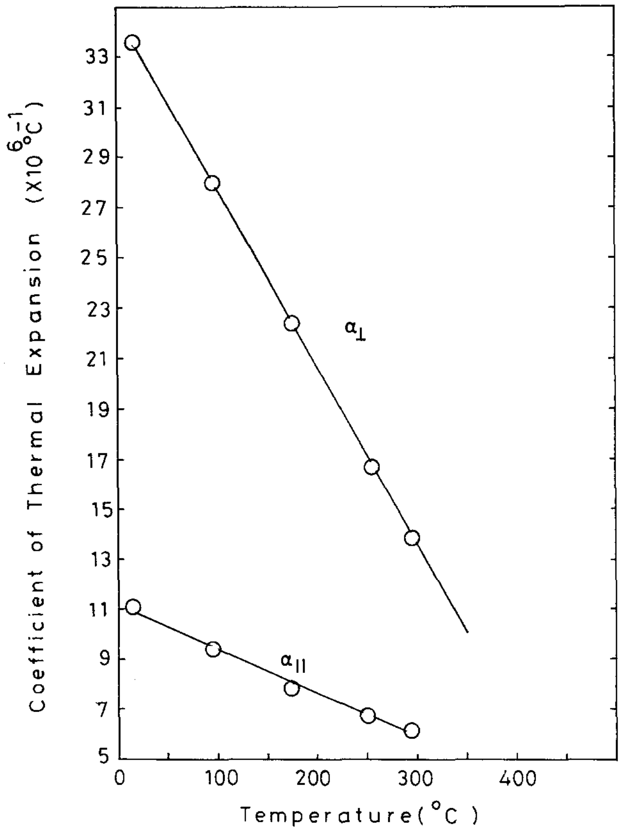

Figure 4 Variation of the coefficients of thermal expansion of $Tl_2Mo_6Se_6$ with temperature.

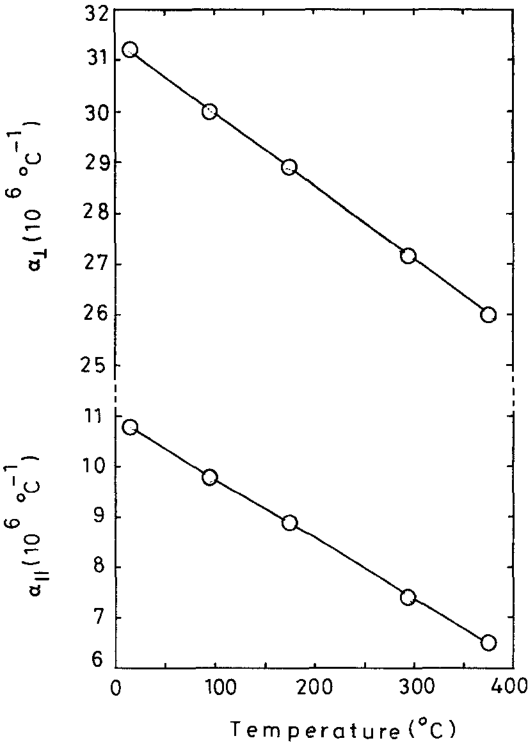

Figure 5 Variation of the coefficients of thermal expansion of $Cs_2Mo_6Se_6$ with temperature.

The three substances are isostructural, with space group $P6_3/m$. The crystal structure of $Tl_2Mo_6Se_6$ has been determined by Potel [10] and the structures of $Cs_2Mo_6Se_6$ and $Na_2Mo_6Se_6$ by Gougeon [11]. As mentioned earlier, the structure is characterized by one-dimensional $(Mo_{6/2}Se_{6/2})^1_\infty$ chains parallel to *c*, separated by parallel chains of M atoms (Fig. 7). The $(Mo_{6/2}Se_{6/2})^1_\infty$ chain is formed by an infinite stack of Mo_3 and Se_3 triangles in staggered positions and may be viewed as the result of a linear condensation of an infinite number of Mo_6Se_6 clusters.

The experimental data on the three compounds is summarized in Table II. The *c* parameter is nearly the same in the three compounds and the *a* parameter progressively increases with the ionic size of M as to be expected. The intra triangle and the inter triangle

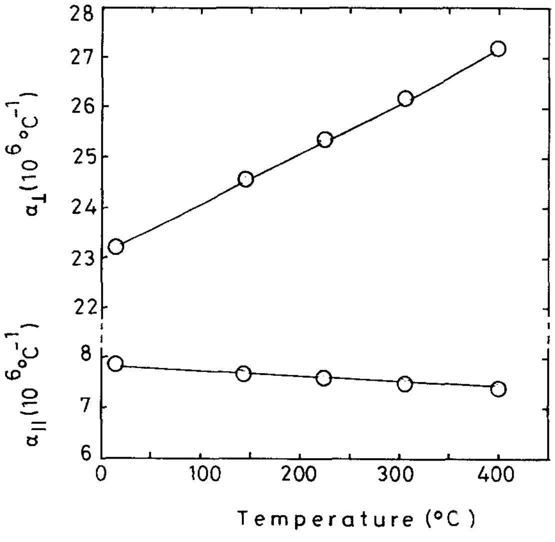

Figure 6 Variation of the coefficients of thermal expansion of $Na_2Mo_6Se_6$.

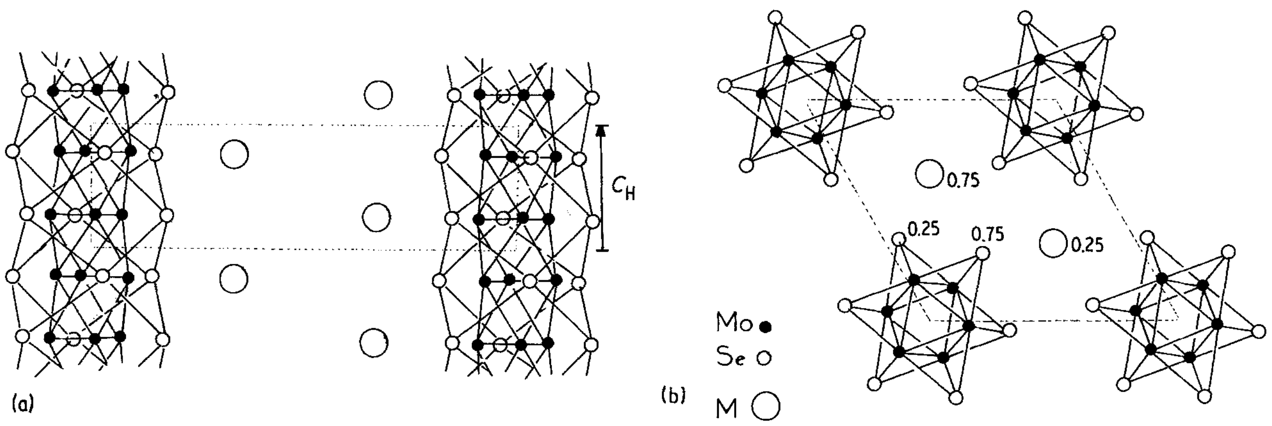

Figure 7 Projection of the structure of $M_2Mo_6Se_6$ on to (a) $(1\,1\,\bar{2}\,0)$ plane, (b) (0 0 0 1) plane.

TABLE II Data on $Tl_2Mo_6Se_6$, $Cs_2Mo_6Se_6$ and $Na_2Mo_6Se_6$

	$Tl_2Mo_6Se_6$	$Cs_2Mo_6Se_6$	$Na_2Mo_6Se_6$
a (nm)	0.8935	0.9548	0.8656
c (nm)	0.4503	0.4497	0.4486
$\alpha_\perp(10^{-6}\,{}^\circ C^{-1})$ at 16° C	33.6	31.2	23.2
$\alpha_\parallel(10^{-6}\,{}^\circ C^{-1})$ at 16° C	11.1	10.8	7.9
Mo–Mo, intra triangle (× 2) (nm)	0.2663	0.2650	0.2658
Mo–Mo, inter triangle (× 4) (nm)	0.2725	0.2722	0.2715
Mo–Mo, inter chain (× 2) (nm)	0.6343	0.6877	0.6122
Mo–Se, intra triangle (× 2) (nm)	0.2611	0.2601	0.2614
Mo–Se, inter triangle (× 2) (nm)	0.2695	0.2695	0.2689
Se–Se, intra chain (× 4) (nm)	0.3767	0.3759	0.3762
Se–Se, inter chain (× 2) (nm)	0.3877	0.4281	0.3769
M–Se (× 3) (nm)	0.3436	0.3614	0.3424
M–Se (× 6) (nm)	0.3400	0.3708	0.3222
M–M, (intra unit cell) (nm)	0.4776	0.5016	0.4656
Ionic radius of M (nm)	0.147	0.167	0.097
Metallic radius of M (nm)	0.155	0.235	0.157

Mo–Mo distances are very close to the Mo–Mo distance 0.2723 nm in molybdenum metal. Hence, the cohesion between the molybdenum atoms in the chain is quite strong and the radius of the molybdenum atom in these compounds may be taken as 0.135 nm i.e. half the Mo–Mo distance. The average intra chain Mo–Se distance is about 0.265 nm. Hence, the atomic radius of selenium in these compounds is about 0.13 nm, which approaches the single bond covalent radius of selenium 0.117 nm. Thus the bonding between molybdenum and selenium in the chain may also be considered as strong.

On the other hand, if the inter chain atomic distances are considered, the Mo–Mo distance is more than 0.6 nm, precluding any coupling between the molybdenum atoms. The inter chain Se–Se distances are about 0.4 nm which are much more than 0.26 nm (twice the atomic radius of selenium in these compounds). The M–Se distances for all the compounds are considerably more than the sum of the ionic radius of M and the radius of selenium. The intra unit cell M–M distance is very large when compared to twice the ionic radius or the metallic radius in all the compounds. Hence, the intra chain atomic bonds are considerably stronger than the inter chain bonds, resulting in a small coefficient of expansion along the c-direction and a large coefficient in the perpendicular direction. It is interesting to note that the value of $\alpha_\parallel$ is close to the coefficient of thermal expansion of molybdenum metal, $5 \times 10^{-6}\,{}^\circ C^{-1}$ [12], lending support to the conclusion by Potel *et al.* [13], that these compounds behave like a one-dimensional metal. The anisotropy in thermal expansion is consistent with the anisotropy in electrical conductivity which has a very large value along the c-axis compared to that in the perpendicular direction.

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