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$_2$Mo$_6$Se$_6$, Cs$_2$Mo$_6$Se$_6$, and Na$_2$Mo$_6$Se$_6$ 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 ($c_s$) is found to be much smaller than that in the perpendicular direction ($c_p$). 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 $M_2$Mo$_6$X$_6$ (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$_{6/2}$)$_2$ 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$_2$Mo$_6$Se$_6$, 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$_2$Mo$_6$Se$_6$, Cs$_2$Mo$_6$Se$_6$ and Na$_2$Mo$_6$Se$_6$.

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 19cm 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 Guinier–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].

$$f(\theta) = -2 \cot \theta \cos \theta \cos (2\theta - x)$$  

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 19cm 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 non-cubic 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$_2$Mo$_6$Se$_6$ 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.

$$a (\text{nm}) = 0.8930 + 0.3017 \times 10^{-4} T - 0.3147 \times 10^{-7} T^2$$  

where $\theta$ is the Bragg angle and $x$ 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, CuK$\alpha$ 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 19cm 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 non-cubic crystals with few space group extinctions and with large lattice parameters.
$Na_2Mo_6Se_6$:  
$a (\text{nm}) = 0.4501 + 0.8029 + 10^{-5}T$  
$-0.1030 \times 10^{-7}T^2$  
$c (\text{nm}) = 0.4490 + 0.3510 \times 10^{-5}T$  
$-0.2128 \times 10^{-9}T^2$  

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$\alpha_i = 11.13 \times 10^{-6} - 1.75 \times 10^{-8}T$  

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, $\alpha_i$ is much greater than $\alpha_1$, 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