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The Thermal Expansion of $2H$-MoS_2, $2H$-$MoSe_2$ and $2H$-WSe_2 between 20 and 800°C

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The hexagonal cell dimensions a and c of $2H$-MoS_2, $2H$-$MoSe_2$ and $2H$-WSe_2 have been measured over the temperature range 20 to 800°C. In all three compounds a and c increased non-linearly with temperature, the linear thermal expansion coefficient of c being greater than that of a. Above 500°C the compounds begin to decompose in vacuum.

Introduction

MoS_2, $MoSe_2$ and WSe_2 are semiconductors (type MX_2) belonging to the large group of compounds which crystallize with a layer structure. Crystals of all three compounds can be grown in the form of large, flexible, hexagonal plates which may be repeatedly cleaved, using adhesive tape, to give very thin crystals having the optic, c, axis normal to the major (00.1) crystal surface. This easy cleavage in (00.1) is evidence of the weak interlayer bonding that exists between the (X–M–X), (X–M–X) sandwich layers from which the crystals are composed.

In MoS_2, $MoSe_2$ and WSe_2 the metal M atom has trigonal prismatic coordination within the layer and a number of structural polytypes are possible depending upon the way in which the layers are stacked one upon the other (Zvyagin & Soboleva, 1967). The most common polytypes are the hexagonal $2H$-MoS_2, where the stacking sequence is $ABA|BAB$ in the $(11\bar{2}0)$ section, and rhombohedral $3R$-MoS_2 where the stacking sequence is $ABA|BCB|CAC$ in the $(11\bar{2}0)$ section; the vertical stroke denotes layer–layer separation.

The trigonal prism coordination of the metal M atom in MoS_2, $MoSe_2$, WSe_2 is attributed to the relative values of the ionic ratio r_+/r_- and the fractional ionic character f_i (Gamble, 1974) where

$$f_i = 1 - \exp\left[-\tfrac{1}{4}(X_M - X_X)^2\right]$$

and X_M, X_X are the electronegativities of the metal and chalcogen atom respectively. An octahedral coordination of the metal M atom occurs in some other MX_2 layer compounds.

The surfaces of MoS_2 crystals grown directly from the powder compound show well defined hexagonal growth spirals (Al-Hilli & Evans, 1972*b*) and X-ray powder lines which can be identified in terms of the $P6_3/mmc$ (D^4_{6h}–MoS_2-type) $2H$ crystal structure. Crystals of MoS_2 grown by bromine vapour transport show triangular surface growth features and the X-ray powder lines correspond to a ($3R$) rhombohedral structure in which, referred to the hexagonal lattice, the a parameter of the unit cell is similar to that of the $2H$ polytype but the c parameter is *ca* 1·5 times as great (Al-Hilli & Evans, 1972*b*).

$MoSe_2$ crystals grown directly from the powder show hexagonal surface growth spirals and the X-ray powder lines correspond to the $2H$ polytype. Crystals grown by bromine vapour transport, however, show surface growth features varying between the hexagonal and triangular forms while the X-ray powder patterns show additional lines due to an admixture of the $3R$ polytype (Evans & Hazelwood, 1971).

WSe_2 crystals grown directly from the powder occur as the $2H$ polytype and show well defined hexagonal growth features (Al-Hilli & Evans, 1972*b*). Crystals grown by bromine vapour transport have the form of thin buckled plates with no obvious growth features; the X-ray patterns however are those of the $2H$ polytype.

The room-temperature d.c. conductivity $\sigma_\perp \perp \mathbf{c}$ (*i.e.* parallel to the sandwich layers) in all three compounds is typically $100\sigma_\parallel$, where $\sigma_\parallel$ is the conductivity in the $\mathbf{c}$ direction. At temperatures above *ca* 500°C the conductivity $\sigma_\perp$ increases rapidly with rise in temperature T (K), the slope m $(=E_t/2k)$ of the linear $\ln \sigma_\perp$ *versus* $1/T$ graphs giving the thermal activation energy E_t (eV). In crystals grown directly from the powder $E_t = 1{\cdot}27 \pm 0{\cdot}06$ eV in n-type MoS_2 (El-Mahalawy & Evans, 1976), $1{\cdot}10 \pm 0{\cdot}05$ eV in n-type $MoSe_2$ (Evans & Hazelwood, 1971) and $1{\cdot}32 \pm 0{\cdot}08$ eV in p-type WSe_2 (Davey & Evans, 1972). These values of E_t are probably the thermal counterparts of the $\mathbf{E} \perp \mathbf{c}$ direct optical energy gaps (77°K) which occur at 1·79171 eV in MoS_2 (Neville & Evans, 1976), *ca* 1·68 eV in $MoSe_2$ (Evans & Hazelwood, 1971) and 1·782 eV in WSe_2 (Bradley, Katayama & Evans, 1972). Energy gaps of this magnitude occur in the band-structure calculations (Bromley, Murray & Yoffe, 1972; Harper & Edmondson, 1971; Huisman, de Jonge, Haas & Jellinek, 1971; Matheiss, 1973; Kasowski, 1973) but the transitions giving rise to the optical absorption have not been positively identified. The optical absorption edge in the $3R$-MoS_2 polytype occurs at a lower energy than in the $2H$ polytype (Clark & Williams, 1968) showing that the weak layer–layer interactions exert a detectable effect on the electron energy-band structure of the crystal.

At room temperature the conductivity $\sigma_\perp$ in all three compounds is greater than that predicted using the preceding values of E_t and it is assumed that the room-temperature conductivity is intrinsic and associated with a, so far undetected, smaller energy gap. It has been suggested (Harper, 1974) that such a small energy gap could occur as a result of unequal layer–layer separations.

The variation in cell dimensions of MoS_2, $MoSe_2$ and WSe_2 with temperature have been measured in order to determine (*a*) whether the $2H$ structure present at room temperature persists to the high temperature of the conductivity measurements, (*b*) the relative importance of electron–phonon interaction and thermal expansion in the observed temperature shift of the fundamental optical absorption edge. The numerical values of the thermal expansion complement the published values of the bulk compressibility of MoS_2, $NbSe_2$, HfS_2 (Flack, 1972).

Compound preparation

The MoS_2, $MoSe_2$ and WSe_2 compounds were prepared from elements having the following purities (%), Mo 99·99, W 99·95, S 99·9999, Se 99·999. Stoichiometric amounts of the powdered elements were introduced into a silica ampoule which was then evacuated to a pressure of less than 10^{-6} torr and vibrated for 30 min to ensure mixing of the powder elements. The mixture was distributed along the length of the horizontal sealed ampoule which was then slowly heated, over a period of 5 h, to a final temperature of 700 °C. The ampoule was maintained at this temperature for 24 h and then allowed to cool to room temperature. The constituents of the sealed ampoule were again vibrated for 30 min before the ampoule was returned to the furnace and maintained in an appropriate temperature gradient (Al-Hilli & Evans, 1972*b*), around 1000 °C, for two weeks. At the end of this time single crystals were found growing from the polycrystalline cake. Quantitative analysis has shown that crystals grown in this way have the correct chemical composition, the only detectable impurity being 0·03 wt % Si.

The single crystals of MoS_2, $MoSe_2$ or WSe_2 were then ground, using a pestle and mortar, into a particle size suitable for filling a 0·3 mm diameter silica X-ray capillary tube.

Experimental method

X-ray powder diffraction patterns (Cu $K\alpha$ radiation) were obtained with a 19 cm Unicam S70 powder camera in which the specimen temperature, within the vacuum furnace, could be varied from room temperature to 1000 °C. The powdered crystal sample was mixed with 99·99% purity gold powder before filling the capillary tube so that the powder pattern consisted of gold and MoS_2 (or $MoSe_2$, WSe_2) diffraction lines. The (rotating) sample temperature was determined from the measured gold unit-cell dimensions and the published values of the gold expansion coefficients (Dutta & Dayal, 1963) in conjunction with the measured cell dimensions of gold at room temperature. Halving the X-ray tube current (normally 11 mA at 22 kV) showed that there was no preferential beam heating of the gold or the compound.

The MoS_2, $MoSe_2$ or WSe_2 powder pattern lines at room temperature were indexed with reference to previously published values of the hexagonal cell dimensions *a* and *c*. Accurate values of *a* and *c* at room and all other temperatures were then obtained by a computer procedure which minimized the difference between calculated and measured $\sin^2\theta$ for all the lines of the powder pattern. Experimental values of *a* and *c* at different temperatures t °C are plotted in Figs. 1, 2 and 3 for MoS_2, $MoSe_2$ and WSe_2. The curves through the experimental points represent the second-order polynomial

$$x_t = x_0 + x_1 t + x_2 t^2, \quad (1)$$

giving the best least-squares fit to the experimental values. Here t is the temperature (°C) and the ratio x_1/x_0 gives the principal linear coefficient of thermal expansion in the *a* or *c* direction. In every case the accuracy of the representation was not improved by using a third or fourth-order polynomial.

Cell dimensions of MoS_2

All the powder lines of MoS_2 at room temperature could be identified in terms of a hexagonal unit cell

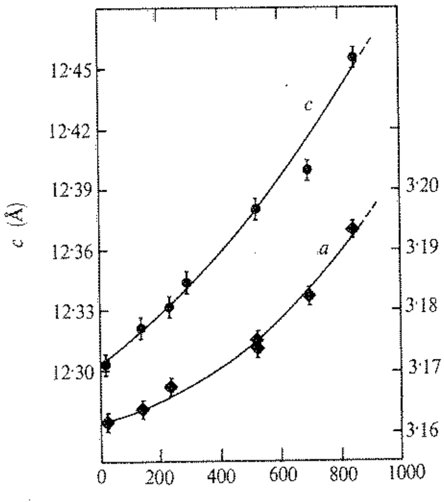

Fig. 1. The cell parameters of $2H$-MoS_2 over the temperature range 20 to 850 °C.

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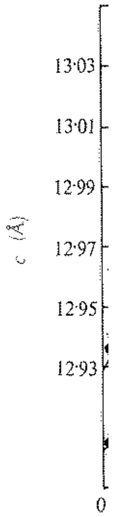

Fig. 2. The cell pa

having dimensions $a=3{\cdot}1622\pm0{\cdot}007$, $c=12{\cdot}301\pm0{\cdot}002$ Å, appropriate to the $2H$ polytype, compared with the previously reported values $a=3{\cdot}160$, $c=12{\cdot}295$ Å (Jellinek, 1962), $a=3{\cdot}140\pm0{\cdot}008$, $c=12{\cdot}327\pm0{\cdot}008$ Å (Al-Hilli & Evans, 1972*b*).

The measured values of a and c for $2H$-MoS_2 at temperatures in the range 20 to 850 °C are given in Fig. 1. The curves through the experimental points giving the temperature dependence of a and c are

$$\begin{aligned} a &= 3{\cdot}1621+0{\cdot}6007\times10^{-5}t+0{\cdot}3479\times10^{-7}t^2 \\ c &= 12{\cdot}3024+0{\cdot}1064\times10^{-3}t+0{\cdot}7737\times10^{-7}t^2, \end{aligned} \quad (2)$$

where t is the sample temperature in °C and the principal linear coefficients of thermal expansion are $\alpha_a=1{\cdot}9\times10^{-6}$/°C and $\alpha_c=8{\cdot}65\times10^{-6}$/°C.

At temperatures around 550 °C extra lines appeared in the MoS_2 powder pattern. These lines persisted to 850 °C, while the MoS_2 lines weakened, at which temperature all the lines (with the exception of the gold lines) disappeared. These same additional lines also appeared in the powder pattern of molybdenum metal around 550 °C and again persisted to about 850 °C. This suggests that the lines are associated with a molybdenum oxide formed by reaction between the metal and the small amount of oxygen present in the vacuum furnace. The additional lines do not match the MoO_3 powder pattern, which disappears around 650 °C as the MoO_3 evaporates, and can only be attributed to one, or more, of the many forms of molybdenum oxide which have boiling points, under vacuum, of about 850 °C.

Cell dimensions of $MoSe_2$

All the lines in the X-ray powder pattern of $MoSe_2$ at 20 °C could be identified in terms of a hexagonal unit cell having dimensions $a=3{\cdot}2920\pm0{\cdot}0007$, $c=12{\cdot}9360\pm0{\cdot}002$ Å which are appropriate to the $2H$ polytype. These room-temperature values of a and c are close to the previously reported values (Å) $3{\cdot}290\pm0{\cdot}002$, $12{\cdot}930\pm0{\cdot}006$ (Evans & Hazelwood, 1971); $3{\cdot}288\pm0{\cdot}001$, $12{\cdot}931\pm0{\cdot}004$ (James & Lavik, 1963); $3{\cdot}288\pm0{\cdot}005$, $12{\cdot}90\pm0{\cdot}005$ (Brixner, 1962); $3{\cdot}2898\pm0{\cdot}0003$, $12{\cdot}921\pm0{\cdot}001$ (Hicks, 1964); $3{\cdot}288\pm0{\cdot}002$, $12{\cdot}92\pm0{\cdot}01$ (Champion, 1965).

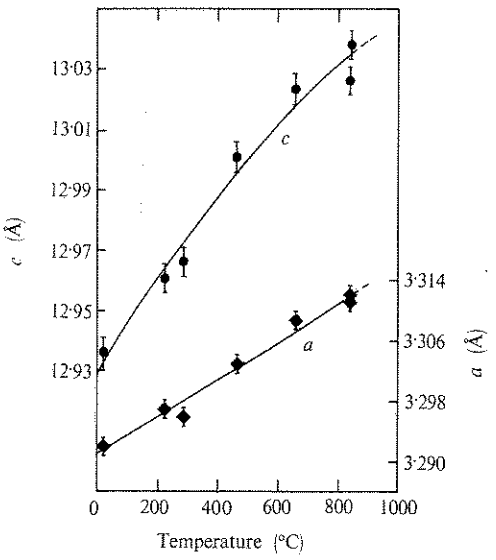

Fig. 2. The cell parameters of $2H$-$MoSe_2$ over the temperature range 20 to 850 °C.

The measured values of a and c at temperatures in the range 20 to 850 °C are given in Fig. 2. The curves drawn through the experimental points are

$$\begin{aligned} a &= 3{\cdot}2910+0{\cdot}2382\times10^{-4}t+0{\cdot}0118\times10^{-7}t^2 \\ c &= 12{\cdot}9288+0{\cdot}1672\times10^{-3}t-0{\cdot}4987\times10^{-7}t^2, \end{aligned} \quad (3)$$

where t is the temperature in °C and the principal linear coefficients of thermal expansion are $\alpha_a=7{\cdot}24\times10^{-6}$/°C and $\alpha_c=12{\cdot}93\times10^{-6}$/°C.

As in the case of MoS_2 additional lines appeared in the $MoSe_2$ powder pattern around 550 °C and persisted, while the $MoSe_2$ lines weakened, to 850 °C at which temperature all the lines disappeared.

Cell dimensions of WSe_2

All the powder lines of WSe_2 at 20 °C could be identified in terms of a hexagonal unit cell having dimensions $a=3{\cdot}2781\pm0{\cdot}0007$, $c=12{\cdot}9505\pm0{\cdot}002$ Å which are appropriate to the $2H$ polytype. Previously published values for WSe_2 are $a=3{\cdot}282\pm0{\cdot}004$, $c=12{\cdot}937\pm0{\cdot}01$ Å (Al-Hilli & Evans, 1972*a*); $a=3{\cdot}29$, $c=12{\cdot}97$ Å (Glemser, Sauer & Konig, 1948).

The measured values of a and c for WSe_2 at temperatures in the range 20 to 670 °C are given in Fig. 3. The curves drawn through the experimental points are

$$\begin{aligned} a &= 3{\cdot}2774+0{\cdot}3630\times10^{-4}t-0{\cdot}1319\times10^{-7}t^2 \\ c &= 12{\cdot}9467+0{\cdot}2165\times10^{-3}t-1{\cdot}107\times10^{-7}t^2, \end{aligned} \quad (4)$$

where t is the temperature in °C and the principal linear coefficients of thermal expansion are $\alpha_a=11{\cdot}08\times10^{-6}$/°C and $\alpha_c=16{\cdot}72\times10^{-6}$/°C, compared with the previously published values $\alpha_a=6{\cdot}8\times10^{-6}$/°C, $\alpha_c=10{\cdot}6\times10^{-6}$/°C (Brixner, 1963).

Additional lines appear in the WSe_2 powder pattern at about 500 °C. These lines match the powder pattern lines of WO_3 which has a higher melting point (1200 °C) than the corresponding molybdenum oxide MoO_3 (m.p. 795 °C). By 700 °C all the WSe_2 powder lines have disappeared leaving just the WO_3 lines.

Discussion

For all three compounds the principal linear coefficient of thermal expansion $\alpha_c>\alpha_a$, which is consistent with the relative inter- and intralayer bond strengths. Similarly the compressibility β of $2H$-MoS_2 (also $NbSe_2$, HfS_2) is greater in the c direction than in the a direction (Flack, 1972).

The cell dimensions of $MoSe_2$ and WSe_2 are similar but according to equations (3) and (4) there is no temperature at which they are the same. The different values of c/a for the two compounds, which have similar ionic ratios, presumably reflect their different ionic character. The thermal expansion ratios α_c/α_a of $MoSe_2$ (1·78) and WSe_2 (1·51) are also different and much smaller than that of MoS_2 (4·55). The changing nature of the interatomic bonding forces in the sequence MoS_2, $MoSe_2$, WSe_2 is presumably also responsible for the change, from positive to negative, in the second-order expansion coefficient, equations (2), (3), (4).

In all three compounds the optical absorption, $\mathbf{E}\perp\mathbf{c}$, begins with direct transitions into an exciton state A_1 at photon energy E, whose temperature dependence is given in terms of the other thermodynamic variables by (Grant, Wilson & Yoffe, 1972)

$$\left(\frac{\partial E}{\partial T}\right)_p=\left(\frac{\partial E}{\partial T}\right)_V-\left[\frac{\alpha_c+2\alpha_a}{\beta_c+2\beta_a}\right]\left(\frac{\partial E}{\partial p}\right)_T. \qquad (5)$$

When the measured values for $2H$-MoS_2 of α, equation (2), $\beta_a=3\times10^{-4}$/kbar, $\beta_c=17\times10^{-4}$/kbar (Flack, 1972) and $(\partial E/\partial p)_T=2\times10^{-3}$ eV/kbar (Grant, Wilson & Yoffe, 1972) are substituted, it is found that the last term in equation (5) is approximately 10^{-5} eV/°K at room temperature. The temperature shift of A_1, *viz* -4×10^{-4} eV/°K (Neville & Evans, 1976) is thus primarily due to the electron–lattice term $(\partial E/\partial T)_V$ with the lattice expansion having comparatively little effect. If the relative values of α and β remain the same for $MoSe_2$, WSe_2 then the same conclusion would hold for these compounds. This would explain why there is no direct correlation between the temperature shift of the absorption edge in MoS_2 [$-0·4$ meV/°K (Neville & Evans, 1976)], $MoSe_2$ [$-0·27$ meV/°K (Evans & Hazelwood, 1971)], WSe_2 [$-0·5$ meV/°K (Bradley, Katayama & Evans, 1972)] and the thermal expansion coefficients of these compounds.

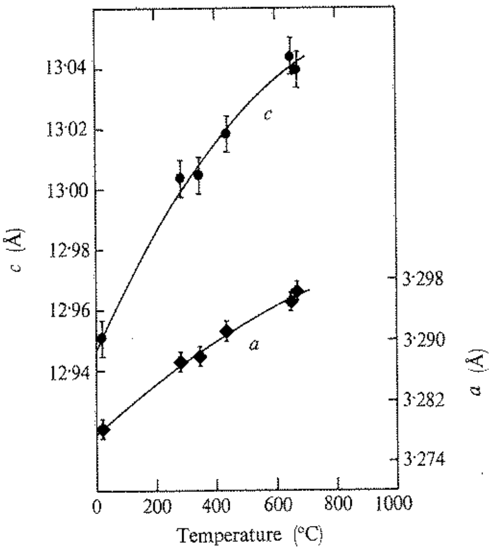

Fig. 3. The cell parameters of $2H$-WSe_2 over the temperature range 20 to 700 °C.

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