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Studies of defects in WSe_2 single crystals

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Abstract. A realistic estimation of growth and deformation fault probability has been made in the crystals of WSe_2 grown by a direct vapour transport method. Electron microscopy of the specimens revealed the presence of two-fold ribbons from which the γ/μ ratio has been determined. Attempts to study polytypism have also been described.

Keywords. Vapour transport; polytypism; dichalcogenide; stacking fault; half width.

1. Introduction

Recently, considerable interest has arisen in the structural, optical, electrical magnetic and superconducting properties of the transition metal dichalcogenides. The diverse physical properties of this broad class of materials have been reviewed by Mooser (1976).

The present paper has been confined to the structural properties of the tungsten diselenide which is a layered dichalcogenide of transition metals from groups VIA of the periodic table. Structurally WSe_2 consists of Se–W–Se sheets in which every tungsten atom is surrounded by six selenium atoms in a trigonal prism. The stacking sequence of the sheets can be symbolised by $A_B\, B_A\, A_B \ldots$ where A_B means a Se–W–Se sheet with the selenium atoms in A positions and the tungsten atoms in the B positions and B_A means a sheet with the selenium atoms in B positions and the tungsten atoms in the A positions. The pronounced layered structure can cause stacking faults in this compound. The stacking fault probability using the method employed by Warren (1959), evidence of the stacking faults by electron microscopy and the search for occurrence of polytypism are studied and described in this paper.

2. Stacking fault probability

Single crystals of WSe_2 used were grown by the sublimation method (Agarwal *et al* 1977). Agarwal and Capers (1976) studied the growth and deformation fault probability in $MoTe_2$ crystals using the formula given by Warren (1959).

$$3\alpha + 3\beta = B_{2\theta}\, \pi^2 c^2 \,/\, 360\, l d^2 \tan\theta \qquad \text{(for } l \text{ even)},$$

$$(3\alpha + \beta) = B_{2\theta}\, \pi^2 c^2 \,/\, 360\, l d^2 \tan\theta \qquad \text{(for } l \text{ odd)},$$

where $B_{2\theta}$ is the full half width of reflection in 2θ degrees, θ the Bragg angle d the interplanar spacing, c is $2d_{002}$, l the miller index, α is the deformation fault probability and β is the growth fault probability.

We use the widths of the fault affecting x-ray reflections in WSe_2 (figure 1) to calculate the growth and deformation fault probability as shown in table 1. The half widths of the faulted reflections have been calculated by eliminating the effects of small domain size and strain by taking the nearest fault-free reflections. The α and β values were 0·0629 and 0·0049 respectively and this implies that the number of deformation and growth faults is 63 and 5 respectively for 1000 atomic layers.

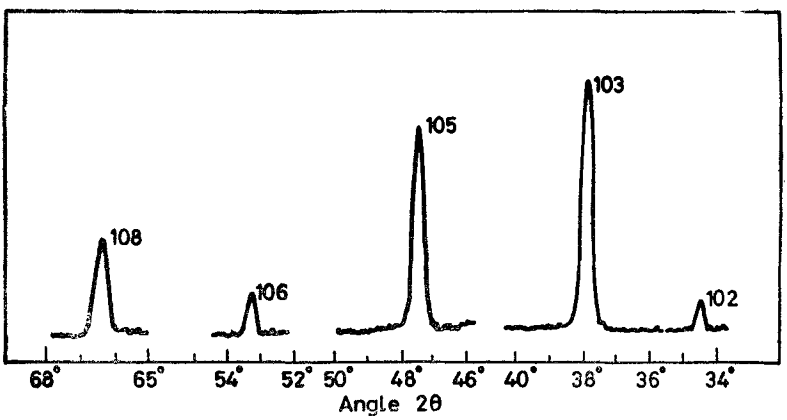

Figure 1. X-ray diffractometer trace obtained from a WSe_2 sample.

Table 1. Deformation and growth fault probabilities.

Reflection hkl	Half width $B^0_{2\theta}$	$3\alpha + 3\beta$	$3\alpha + \beta$	Mean $3\alpha + 3\beta$	Mean $3\alpha + \beta$	α	β
102	0·185	0·2044	..	..	..	..	..
103	0·24	..	0·1917	0·2035	0·1937	0·0629	0·0049
105	0·34	..	0·1957	..	..	..	..
106	0·39	0·2033	..	..	..	..	..
108	0·455	0·2037	..	..	..	..	..

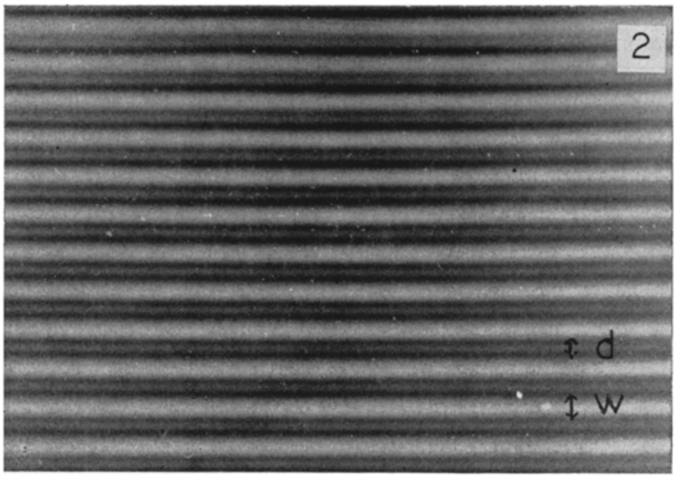

Figure 2. Two-fold ribbon pattern oriented in the basal plane of WSe_2 ($\times$ 45000).

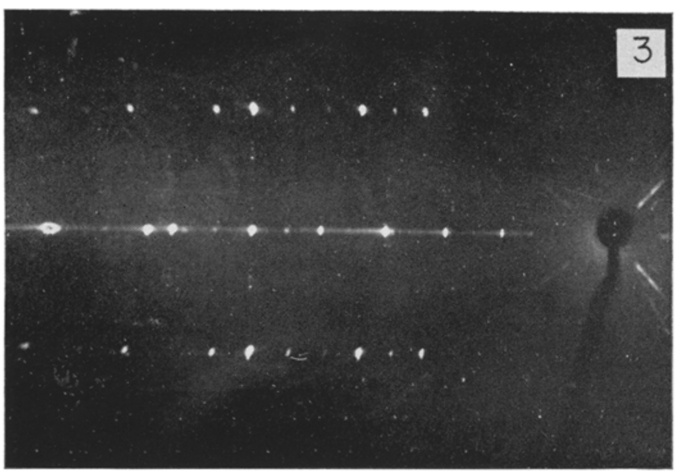

Figure 3. X-ray oscillation photograph.

3. Stacking faults using transmission electron microscopy

To confirm the presence of stacking faults, crystals were selected from the same initial stock of material as that used for x-ray diffractometer studies. Specimens sufficiently thin to transmit electrons were prepared by repeated cleavage with an adhesive tape.

Figure 2 is a typical transmission electron micrograph showing stacking faults made visible by the characteristic interference bands which run parallel to the surface of the foil. This figure is representative of several such features observed in our study.

The γ/μ value (where $\gamma=$ stacking fault energy and $\mu=$ shear modulus) was determined from the geometry of the two-fold patterns in figure 2 using the expression given by Amelinckx and Delavignette (1962)

$$\gamma=\left[\frac{3A-B}{4d}\,q\pi\right]\cos q\pi$$

where $A=\dfrac{\mu b^2}{2\pi(1-\nu)}$, $\quad B=\dfrac{\mu b^2}{2\pi}$,

$$q=d/(d+w),$$

d and w are as shown in figure 2, ν is the Poisson's ratio and b the magnitude of the Burger's vector for the partial dislocation.

Since μ is not known for WSe_2, γ/μ which is proportional to γ was calculated. The value of b was $1\cdot 90\times 10^{-6}$ cm. For the ribbon pattern, figure 2, d and w were found to lie in the ranges $4\cdot 968\times 10^{-6}$ cm to $5\cdot 868\times 10^{-6}$ cm and $9\cdot 497\times 10^{-6}$ cm to $10\cdot 42\times 10^{-6}$ cm, respectively. The corresponding values of γ/μ were found to lie between $3\cdot 078\times 10^{-12}$ cm to $3\cdot 275\times 10^{-12}$ cm.

4. Polytypism

Since the presence of stacking faults plays a decisive role in the growth of polytypism, the low value of the stacking fault energy determined above and the presence of stacking faults evidenced by the x-ray studies suggest the presence of profuse polytypism in these crystals.

Figure 3 shows an *a*-axis oscillation photograph corresponding to one face of the crystal taken with CuKα radiation employing conventional x-ray tube. The oscillation started from the position in which the *c*-axis (perpendicular to the crystal flake) made an angle of 25° with the incident x-ray beam and was carried to the position (25° + 15°) 40°, i.e. the oscillation range was $32\cdot 5°\pm 7\cdot 5°$. This is the range in which almost all the reflections of $10.l$ or $01.l$ types are recorded for any type of WSe_2 polytypes. Figure 3 shows that there are a large number of discrete spots on the layer lines. It has been verified from actual calculations that the discrete spots correspond to the basic 2H structure. However, there are also some additional spots other than those obtained for the basic 2H structure. In fact one can even notice the presence of some weak spots between two consecutive 2H spots. This indicates the possibility that the crystal face under investigation is a matrix of 2H and higher polytypes.

5. Conclusions

(i) The stacking fault probability measurements indicate the presence of stacking faults which has been confirmed from electron microscopic observations.
(ii) The growth fault probability in these crystals is less than the deformation fault probability.
(iii) The low values of γ/μ suggests that the stacking fault energy is small.
(iv) The studies on polytypism reveal that the crystals of WSe_2 are primarily of 2H type.

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