

# Line broadening studies of deformation in $\text{MoTe}_2$

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Deformed (cold-worked) samples of molybdenum ditelluride ( $\text{MoTe}_2$ ) – a six-layered hcp structure – have been found to exhibit symmetrical broadening in their X-ray diffraction profiles corresponding to  $H - K = 3N \pm 1$  reflections. Integral breadth measurements have been used to analyse the line profiles in a manner as it is applicable to a simple two layered hcp structure. The reason for such a mode of approach has been discussed.

On the presumption that the growth faults in this material are negligibly small, the deformation stacking faults probability due to the glide on Te/Te slip planes only is found to be  $\simeq 0.144 \pm 0.010$ , and the dislocation density in the bulk material is estimated to be  $\simeq (2.66 \pm 0.36) \times 10^{11} \text{ cm cm}^{-3}$ .

## 1. Introduction

Molybdenum ditelluride has been classified, according to the crystallographic information [1], as a hexagonal structure belonging to space group  $P6_3/mmc$  ( $D_{6h}^{4\text{h}}$ ). It contains two molecular units in the unit cell. The configuration of six tellurium atoms about each molybdenum atom in this crystal is not octahedral, but is that of a trigonal prism: the molybdenum atom is located at the centre of a trigonal prism where the corners are occupied by tellurium atoms. This arrangement places molybdenum atoms on two vertical axes and the pairs of tellurium atoms are also on the same vertical axes with one tellurium atom above and one below each molybdenum atom. Therefore, a molybdenum layer is sandwiched between two layers of tellurium atoms, thus forming three layered blocks. These blocks are so situated on one another that every third one repeats the first, every fourth the second, etc.

The compound is isomorphic with molybdenite, hence the hcp stacking of two kinds of atoms may be described following Pauling's [2] notations by a sequence given below.

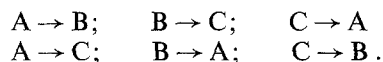
Te(a) Mo( $\beta$ ) Te(a) Te(b) Mo( $\alpha$ )  
Te(b) Te(a) Mo( $\beta$ ) Te(a) Te(b) . . . ,

where a and b refer to tellurium positions and  $\alpha$  and  $\beta$  refer to molybdenum positions.

Since tellurium shows a largely non-metallic chemistry, its compounds are similar in nature to

those of selenium and sulphur. The covalent bonds between molybdenum and tellurium atoms in  $\text{MoTe}_2$  are much stronger than the Van der Waal's forces between the two adjoining tellurium layers. Therefore, one expects the glide on Te/Te slip planes to take place much easier than the glide on Mo/Te slip planes.

Glide operation on Te/Te slip planes introduces "deformation or transformation" stacking faults which not only changes the arrangement (hexagonal or cubic) of the layer in which it occurs but also those of the subsequent layers. Symbolically, we have:



The letters A, B and C represent three different positions of a close-packed structure. This type of fault can be produced either during plastic deformation or during certain phase transformation or even spontaneously at an appropriate temperature.

Cold-work changes the diffraction pattern of metals, alloys and many other polycrystalline materials by varying the position of and broadening the X-ray powder pattern peaks. Plastic deformation of polycrystalline materials also produces structural changes that influence the physical properties of the material, e.g. the deformation forces introduce lattice stress and generate dislocations and stacking faults and

these parameters bear a close relationship with the changes observed in X-ray powder diffraction peaks.

The changes in the position of powder pattern peaks may be attributed to residual stresses in bulk specimen [3, 4], to faulting and to lattice parameter changes due to dislocations and segregation of solute atoms [3, 5, 6]. The peak-shift produced by faulting and residual stresses vary with crystallographic directions. The broadening of peak profiles [5, 7] is assumed to be produced by a reduction of size of the coherently diffracting domains (crystallite size), by faulting on certain ( $HKL$ ) planes and by distortion within the crystallites (lattice strain). The broadening produced by small crystallite size and by stacking faults is independent of the order of reflections but a noticeable difference between them is that the crystallite size affects all reflection points whereas the stacking faults influence only certain reflections.

Stacking disorders have also been found in layer structures like mica [8] and graphite [9]. Various solid rare gases and their solid solutions with fcc and hcp structures and Van der Waal's binding [10, 11] also show the existence of stacking faults. They may occur in crystals as grown but are far more common after deformation or after a phase transformation of martensitic type.

In hcp materials, both growth and deformation faults are possible on (0002) planes. There is, however, no peak shift and/or no peak asymmetry except for a symmetrical peak broadening as a result of either of these faults. The symmetrically broadened peaks correspond to the reflections  $H - K = 3N \pm 1$ , where  $H$ ,  $K$  and  $L$  are Miller indices of the diffracting planes and  $N$  is zero or an integer. The magnitude of broadening is different for the lines that are "even" or "odd" with respect to the index  $L$  of the diffracting plane.

## 2. Experimental procedure

The material, molybdenum ditelluride, was obtained from M/s Research Organic/Inorganic Chemical Corp., California, USA. It was deformed at room temperature ( $\approx 26^\circ\text{C}$ ) by powdering it in an agate-mortar. The powder was then screened through 300 mesh classifiers and compacted to the desired shape for the sample holder of an X-ray diffractometer. A diffractometer was used to record X-ray diffraction profiles with Ni filtered  $\text{CuK}\alpha$

radiations and a scanning speed of  $\frac{1}{8}^\circ$  per minute. The aberration due to instrumental broadening inherent in the recorded profiles of the deformed samples was eliminated by using the integral breadths of the X-ray diffraction profiles of a vacuum-annealed powder of zirconium. The integral breadth due to stacking faults was computed after removing the effects of domain size and strain broadening using the  $H - K = 3N$  reflection as a standard.

## 3. Integral breadth measurements

The integral breadth of  $K\alpha_1$  profile of each reflection was calculated. Rachinger's method [12] was used to separate the  $K\alpha_1$  component from the composite doublet  $K\alpha_1\alpha_2$ . Instrumental broadening effect from all such  $K\alpha_1$  profiles was removed by using the following relation [13].

$$\beta = B - \frac{b^2}{B},$$

where  $B$  is the integral breadth of  $K\alpha_1$  part of a recorded profile,  $b$  is the instrumental broadening and  $\beta$  is the integral breadth of  $K\alpha_1$  profile free from instrumental broadening.

From chart-recorded diffraction profiles (10 $\bar{1}$ 3), (0006) and (10 $\bar{1}$ 5) as shown in Fig. 1, the integral breadth,  $\beta_F$ , due to the stacking faults only can be separated out by using the following formula [13]

$$\beta_F = \beta - \frac{\beta_s^2}{\beta},$$

where  $\beta$  refers to the integral breadth values corrected for instrumental broadening and the subscript  $s$  refers to the integral breadth value of a standard profile, corresponding to the reflection (0006) in the present work.

$\beta_F$  is related to the deformation fault probability  $\alpha_D$  and growth fault probability  $\alpha_G$  by the following approximations [14] when both types of fault co-exist and the deformation is rather heavy.

$$\beta_F = \frac{\alpha_D + \alpha_G}{4 - 3\alpha_D - 3\alpha_G} \frac{6\lambda Ld}{c^2 \cos \theta},$$

for  $H - K = 3N \pm 1, L$  even

$$\beta_F = \frac{3\alpha_D + \alpha_G}{4 - 3\alpha_D - 3\alpha_G} \frac{2\lambda Ld}{c^2 \cos \theta},$$

for  $H - K = 3N \pm 1, L$  odd.

$$\beta_F = 0, \quad \text{for } H - K = 3N,$$

where  $\lambda$  is the wavelength of X-radiation,  $\theta$  is

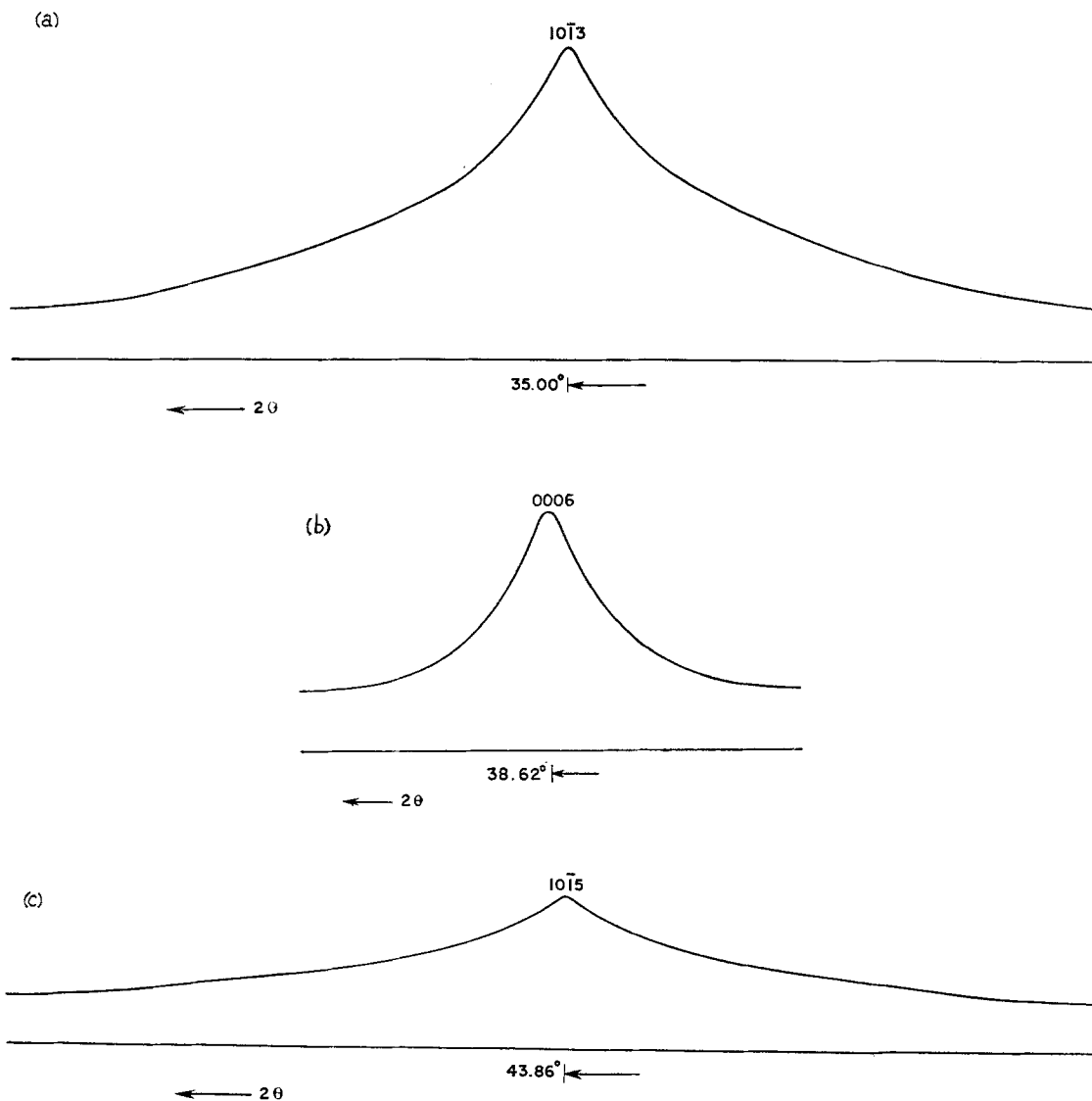


Figure 1 X-ray diffraction profiles of (a) (10 $\bar{1}$ 3), (b) (0006) and (c) (10 $\bar{1}$ 5) reflections.

the Bragg angle,  $d$  is the interplanar spacing of  $HKiL$  plane and  $c$  is the lattice parameter.

If the growth faults are negligibly small,  $\alpha_G = 0$ , we can write,

$$\beta_F = \frac{\alpha_D}{4 - 3\alpha_D} \frac{6\lambda LD}{c^2 \cos \theta},$$

for  $H - K = 3N \pm 1$ ,  
 $L$  odd or even.

The following equations have been used to calculate the domain size ( $D$ ) and lattice strain ( $\epsilon$ ) values.

Wagner and Aqua [15]:

$$\left(\frac{\beta \cos \theta}{\lambda}\right)^2 = \frac{1}{D^2} + \left(\frac{4\epsilon \sin \theta}{\lambda}\right)^2;$$

Hall [16]:

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{4\epsilon \sin \theta}{\lambda};$$

Halder and Wagner [17]:

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{16\epsilon^2 \sin^2 \theta}{\beta \lambda \cos \theta}.$$

The latter empirical formula is found to yield domain size and lattice strain values in close

agreement with those obtained by the Wagner-Aqua method and also with those obtained by Fourier analysis procedures.

The dislocation density is related to the domain size by a formula  $\rho_D = 3/|D|^2$  based on the Williamson and Smallman model [18].  $\rho_D$  is defined as the total length of the dislocation line per unit volume and is independent of the distribution of dislocations in the material.

#### 4. Results and discussion

Domain size and lattice strain values were calculated from the three standard plots [15-17] and are shown in Fig. 2a, b and c. A common characteristic of all these plots is that the points corresponding to the reflections  $H - K = 3N$  lie on or cluster around a straight line fitted by the

least squares method, whereas the points with  $H - K \neq 3N$  are distinctively shifted from the line and this makes a basis for the calculation of the stacking fault probability. The domain size parameter has been also used to estimate the dislocation density in the material (Table I).

In evaluating stacking fault probability, we consider only deformation faults arising out of a glide between two adjoining layers of non-metal atoms bound by the weak Van der Waal's forces. The probable occurrence of a glide between molybdenum and tellurium, or any other glide in which the covalent bonds are no longer conserved, is not considered. Such a glide, however, cannot be completely ruled out even though the rearrangement of the covalent network involves a high expense of energy. Although X-ray line broadening studies furnish no evidence as to the existence of low or high energy stacking faults, a high value of stacking fault probability *ipso facto* suggests the presence of low energy stacking faults.

The resemblance of  $\text{MoTe}_2$  - a six layered hcp ( $6H$ ) structure - with that of a simple hcp ( $2H$ ) structure may be considered as follows: the unit cell of this compound contains two molecular units of six atoms, two of molybdenum

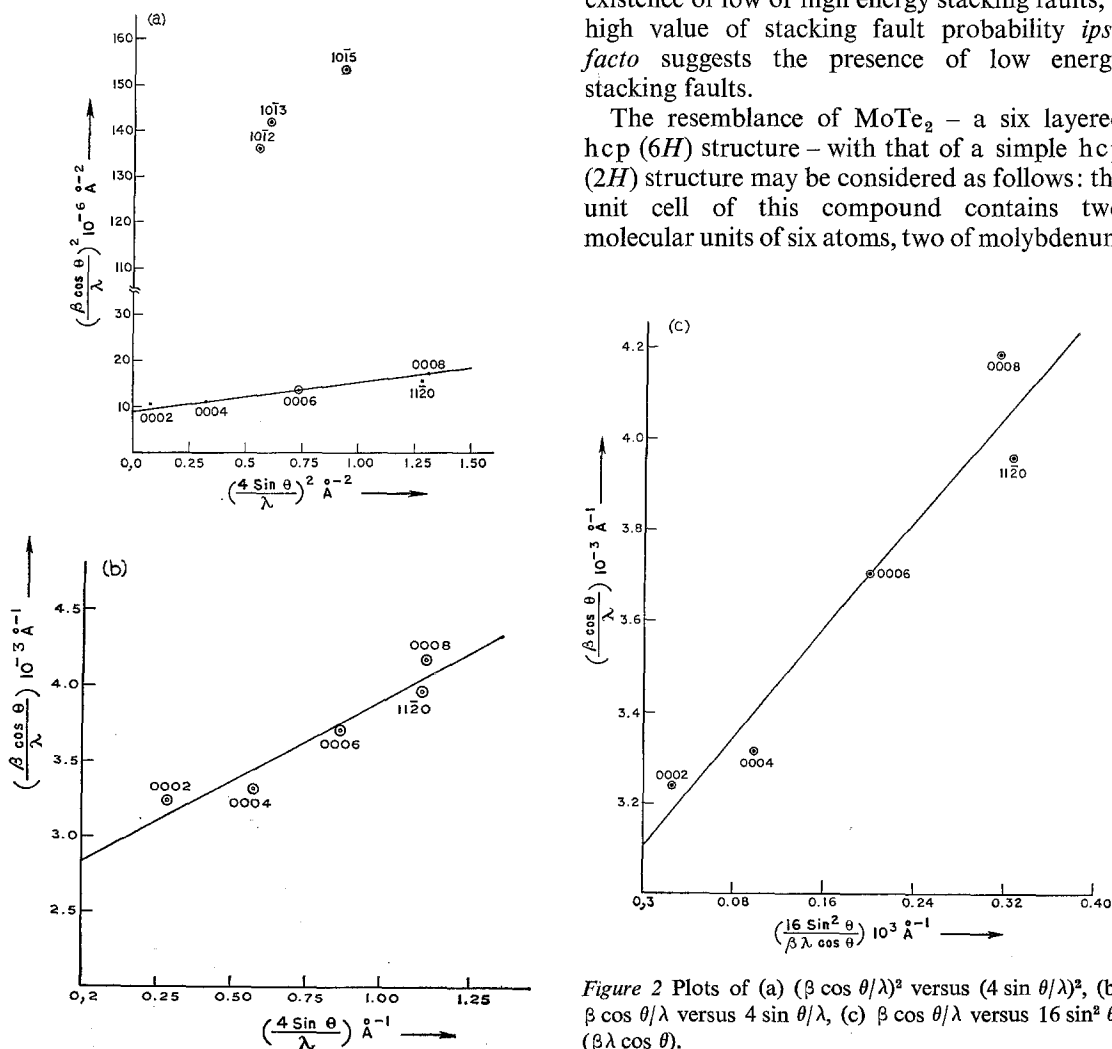


Figure 2 Plots of (a)  $(\beta \cos \theta / \lambda)^2$  versus  $(4 \sin \theta / \lambda)^2$ , (b)  $\beta \cos \theta / \lambda$  versus  $4 \sin \theta / \lambda$ , (c)  $\beta \cos \theta / \lambda$  versus  $16 \sin^2 \theta / (\beta \lambda \cos \theta)$ .

TABLE I Results of X-ray line broadening in MoTe<sub>2</sub>

Domain size and lattice strain distribution	Domain size $D$ (Å)	Lattice strain $\epsilon$ ( $10^{-3}$ )	Dislocation density, Deformation fault probabilities, $\alpha_D$
Domain size – Cauchy Lattice strain – Cauchy (Hall)	352.1	1.05	2.42
Domain size – Gaussian Lattice strain – Gaussian (Wagner-Aqua)	333.3	2.50	2.70
Domain size – Cauchy Lattice strain – Gaussian (Halder-Wagner)	322.6	1.73	2.88
$\alpha_D$ ( $10\bar{1}3$ )			0.160
$\alpha_D$ ( $10\bar{1}5$ )			0.128
Average values	$336 \pm 24$	$1.76 \pm 0.13$	$2.66 \pm 0.38$ $0.144 \pm 0.010$

and four of tellurium. The compound has weak Van der Waal's binding between the two adjoining Te—Te layers whereas Mo—Te are held strongly by the covalent bonds. Therefore, it may be argued that the Te/Te glide is the most probable, the deforming force being relieved by a relative shift between the two identical molecular blocks Te—Mo—Te/Te—Mo—Te. It is not, therefore, unreasonable to visualize a molecular block as the rigid unit equivalent to one complete layer and the blocks being arranged in an hcp ( $2H$ ) stacking. On the basis of this block-shift scheme, hcp ( $2H$ ) theories would be the closest applicable to these compounds, as discussed by the author [19].

Furthermore, Verble and Wieting [20] carried out an experimental investigation of long wavelength optical phonons in the hexagonal layer structure MoS<sub>2</sub> – a compound isomorphous with MoTe<sub>2</sub> – and observed the degeneracy of mutually exclusive infra-red and Raman active modes. They concluded that a Van der Waal's type of interaction existed between the adjoining S—S layers and used a single layer approximation for the analysis of their results, i.e. a molecular block (unit) in which a molybdenum sheet is sandwiched between the two sulphur sheets. For  $2H$  polytypic behaviour of these structures, the repeat distance includes two such layers. They also suggest similar considerations apply to all the layered structures with more than one such layer in the unit cell.

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Received 3 July and accepted 26 November 1973.