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Dislocation loops in tungstenite (WS_2) crystals

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Abstract. TEM studies of tungstenite crystals grown by sublimation method have been investigated. Dislocation loops observed during such studies have been reported. It has been shown by different methods that these loops have a vacancy character.

Keywords. Tungstenite crystals; dislocation loops; vacancy loops.

1. Introduction

Tungstenite (WS_2) is an isomorph of molybdenite. It belongs to a class of group VI dichalcogenides having C7 type crystal structure which possess a layered structure. These MX_2 (M = W or Mo, X = S, Se or Te) compounds form a structurally and chemically well defined family. The basic structure of loosely coupled X - M - X sheets makes such materials extremely interesting in that they are very remarkably weak between adjacent layers. As a result the crystals have an easy basal cleavage. This compound has attracted considerable attention due to its use in the construction of regenerative electrochemical solar cells.

Dislocations in molybdenite (MoS_2) have been studied independently by Pashley and Presland (1960), Boswell (1960), Kamiya *et al* (1960), Amelinckx and Delavignette (1962), and Agarwal and Babu Joseph (1975).

Recently imperfections in $MoSe_2$ crystals have been reported by Agarwal *et al* (1979b). But to our knowledge no transmission electron microscopic (TEM) studies of WS_2 have been reported. This may be because of the non-availability of these crystals. We have been able to grow them by sublimation method in this laboratory (Agarwal *et al* 1979) and we have made TEM studies of these crystals. During such studies we have come across the striking observation of dislocation loops. The natures of these loops have been studied and described fully in this paper.

2. Experimental

Specimens for transmission electron microscopic studies were prepared by repeated cleavage (Agarwal and Babu Joseph 1974). The specimens were examined in an electron microscope (EF 4 Carl–Zeiss Jena) at an operating voltage of 65 kV.

3. Results and discussion

Figure 1 shows a striking example of dislocation loops. It is clear from the photograph that the interior of the loops exhibits contrast. The contrast can either be in the form of a difference in shade from the surrounding regions or of a set of interference fringes parallel to the foil surface (figure 2). The shade contrast will occur more frequently because the foil surface is always nearly parallel to the basal plane which is also the plane of the loop. Fringes will appear only when the loop plane is inclined with respect to the surface. Sometimes when the loop plane is in the vicinity of a plane of maximum diffracted amplitude, it will exhibit no contrast. When the orientation of the foil is changed, it is seen that the Bragg reflection responsible for producing the contrast also changes and as a result the loop which did not show any contrast originally may exhibit strong contrast and *vice versa*.

In addition to the contrast within the loop the dislocation ring forming the loop also exhibits strong contrast effects. With the change in the orientation of the foil the dislocation loops sometimes have a uniform contrast and sometimes a non-uniform contrast.

The contrast generally arises from two sources, firstly from the dislocation line itself and secondly from the stacking fault contained within the loop. Examples of loops exhibiting all the features mentioned above have been given below. A careful study of the electron micrograph shown in figure 1 reveals that,

(i) The loops are of different sizes marked as (A, B, C, D and E), (ii) Loops (A, B, C, D and E) have a uniform dark contrast within them, (iii) Loops (F and G) have a light contrast within them, (iv) Loops (A, B and C) show the line contrast as well as the stacking fault contrast, (v) Loops (D and G) show only the stacking fault contrast but no line contrast.

Since the contrast in the loops is very sensitive to variation in the specimen, it is seen that upon tilting the region shown in figure 1a clockwise by 7° and 9° figures 1 b, c are produced. It can be noticed in figure 1 b that the stacking fault contrast exhibited by all the loops in figure 1a has changed considerably. Loops (D and G) which were only showing the stacking fault contrast, also show the line contrast. In figure 1a it is interesting to note that some of the loops (A, F and G) are going out of contrast and a few are showing only a partial line contrast. This absence of contrast in the loops (B, C and D) can be explained schematically by figure 2, where figure 2a shows two loops A and B having contrast before changing the inclination and figure 2b shows the same two loops exhibiting no contrast upon tilting.

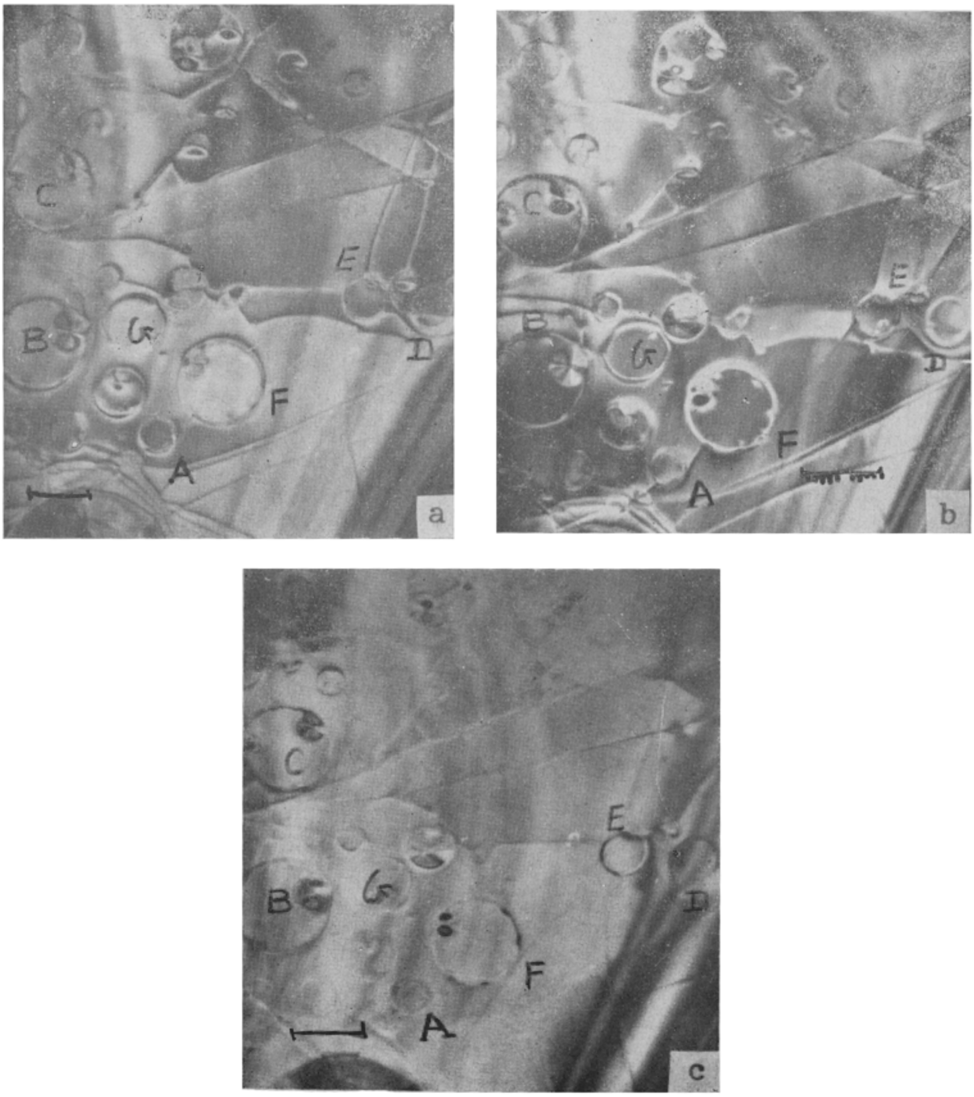

Figure 1 **(a)** Dislocation loops, **(b)** Figure (1 a) at 7° tilt **(c)** Figure 1 **(a)** at 9° tilt Bar = 10.5 μm.

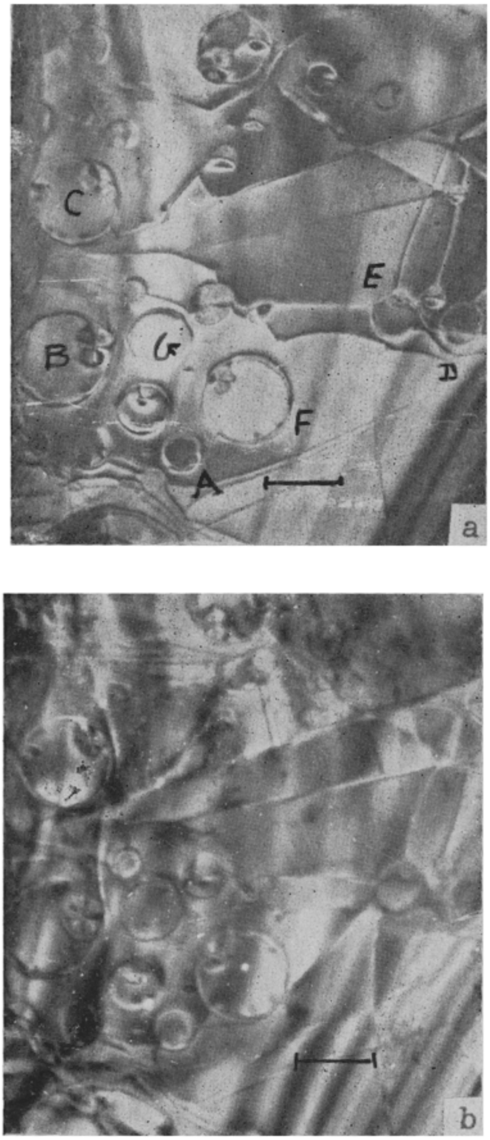

Figure (3) **(a)** **Bright field** images of the dislocation loops **(b)** Dark field images of the region of figure 3 (a) Bar = 10. 5 μm

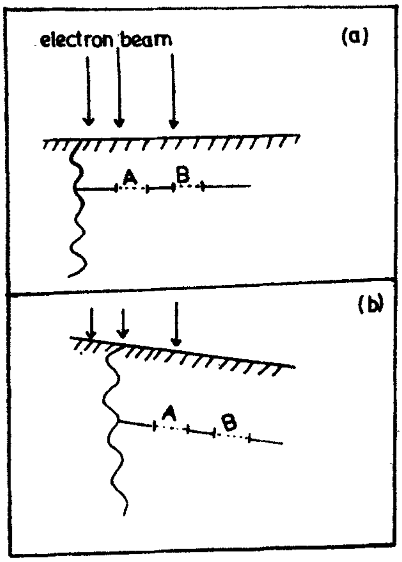

Figure 2. Schematic diagram for showing loop contrast (a) for contrast and (b) for no contrast.

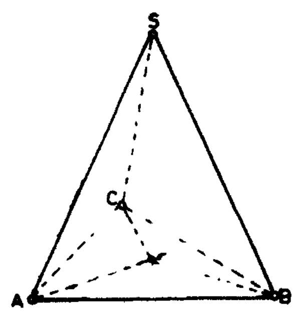

Figure 4. Schematic diagram showing the AS type of the loops.

Figures 3a and b show bright field and dark field images of the dislocation loops. Here it is seen that the loops marked (A, B and C) show the residual contrast as observed by Van Tendeloo *et al* (1974). Now since the loops will show residual contrast only if their Burger's vector is parallel to the diffracting plane, we can conclude that the Burger's vector in the present case is not perpendicular to the loop plane, but is inclined *i. e.* along a direction of the type as shown in figure 4. According to Van Tendeloo *et al* (1974) loops showing the characteristic features mentioned above are vacancy loops. In order to confirm this unambiguously the following experiment was also carried out.

The region shown in figure 1a was tilted at various angles and it was noticed that there was an increase in the projected width of the loops as the angle of inclination was increased in a clockwise manner, thus suggesting that the loops were formed due to a planar array of vacancies.

In order to further support this conjecture, the method adopted by Hall (1974) has been used. According to him the critical radius R_c of a loop (when the energy associated with a prismatic loop resulting from the precipitation of a layer of interstitials) is given by

$$R_c = \frac{1}{12(1-\nu)\pi} \cdot \frac{G}{\gamma} \cdot a^2 \ln\left(\frac{R}{r_0}\right).$$

using the values (Siems *et al* 1964): $R = 5 \times 10^{-5}$ cm, $r_0 = 5 \times 10^{-8}$ cm, $\nu = 0.33$, $\gamma = 1 \times 10^{-12}$ cm, $a = 3.154 \times 10^{-8}$ cm. We get $R_c = 2.85 \times 10^{-4}$ cms.

Since practically all the loops observed are smaller than the critical size, it is conjectured that most of them are vacancy type loops.

4. Conclusions

A striking example of dislocation loops has been given. It has been shown by different methods that these loops are in fact vacancy loops.

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