Electron-Induced Decomposition of Tin (IV) Sulphide in the Electron Microscope

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A combination of selected-area electron diffraction and the new technique of ‘real-space crystallography’ has been used to monitor the electron-induced decomposition of tin (IV) sulphide. In contradiction to the results of other workers, the final product of the decomposition was found to be SnS, while at an intermediate stage, platelets of SnS were formed with (010)SnS parallel to (001)SnS2.

Introduction

Since the early work of Lee, Said & Davis (1969) on negative resistance and switching effects in SnS2, several theories have been put forward to explain these properties. It has been suggested (e.g., Romeo, 1973) that electronic effects produce conducting filaments through the otherwise insulating SnS2. At high currents, local heating then produces structural changes in the filaments and the device is returned to a high-resistance state until a new filament is created.

In order to investigate the decomposition of SnS2 by local heating, we examined specimens of SnS2 in the transmission electron microscope and heated the specimens in situ with the electron beam. This experiment had previously been conducted by Günter & Oswald (1969) but, as we shall show, several inconsistencies were present in their interpretation of the results. Therefore, we repeated their experiments and monitored the structure changes with a combination of selected-area electron diffraction and the powerful new technique of ‘Real-Space Crystallography’ (Steeds, Tatlock & Hampson, 1973; Tatlock & Steeds, 1974). We concluded that SnS was the final product of the decomposition and not β-tin as had been suggested by Günter & Oswald (1969). We were also able to reinterpret all their previous results on the decomposition of SnS2 in this light.

Experimental

Suitable specimens ~600 Å thick were cleaved from platelets of SnS2 which had been synthesized from their elements by an iodine vapour-transport technique (Lee et al., 1969). A JEOL 100 U microscope equipped with a goniometer stage was used throughout the work at a nominal operating voltage of 100 kV. The behaviour of the specimens, as they were heated with the electron beam, was similar to that described by Günter & Oswald. The image first became mottled and then the specimens appeared to melt and recrystallize leaving rectangular cavities. When the specimens were later removed from the microscope, it was observed that the colour of the heated regions had changed from pale yellow to black.

Real-space crystallography

The decomposition of SnS2 by the electron beam was monitored by a combination of selected-area electron diffraction and real-space crystallography. As explained by Steeds et al. (1973), all the information in the diffraction pattern from an electron microscope is also present in the form of bend extinction contours in the image of a bent specimen. By plotting out the contours on a stereographic projection it is possible to deduce the point group of a crystal and from detailed observation of zone-axis patterns where contours intersect, space-group information may be obtained. Finally it is possible to derive information about the types or positions of atoms in a crystal by using many-beam dynamical theory to produce detailed simulations of the contours.

One very useful aspect of this technique connected with space-group determination is the identification of spots in diffraction patterns which are produced by double diffraction. Misleading results may be obtained when a spot in the diffraction pattern which is kinematically forbidden is still excited by the dynamic interaction of two other allowed reflexions. Examination of the dark-field contour corresponding to the spot in question, however, immediately resolves the problem. A contour corresponding to a kinematically allowed reflexion will appear as a bright line connecting all the positions in the crystal which are at the correct orientation for Bragg reflexion. The equivalent image in a double-diffraction spot will only contain a small weakly excited region where two different reflexions are summing with the correct phases. Hence double diffraction effects may be quickly and easily identified by this technique and a good example for α-N2 is discussed by Venables & English (1974).
Fig. 1. Diffraction patterns and proposed indexing of a decomposed specimen of SnS₂ (a) Basic pattern. (b) The same pattern after defocusing the diffraction lens. (c) Indexing in terms of β-tin (after Günter & Oswald). (d) Indexing in terms of SnS.
Identification of the final product of the decomposition

Selected-area diffraction from the recrystallized material gave sharp diffraction patterns which could not be indexed in terms of the SnS$_2$ structure. One such pattern is shown in Fig. 1(a) and a similar pattern obtained by Günter & Oswald (1969) was indexed by them as the [001] pattern of β-tin [Fig. 1(c)]. Although 110 reflexions are kinematically forbidden in this structure, they suggest that double diffraction from, e.g., the 321 and 2T1 reflexions may produce a 110 spot. If this pattern was due to β-tin, however, the 220 and 220 reflexions should be equally excited and this is clearly not the case in Fig. 1(a). Secondly, Fig. 1(b) illustrates the corresponding low-magnification images which were obtained by slightly defocusing the diffraction lens. This shows that the 110 and 1T0 reflexions are not equivalent and higher-magnification dark-field images confirm that the 110 spot is indeed produced by double diffraction but that the 1T0 spot is a conventional dark-field reflexion. Finally, the symmetry of the bright-field contours at this pole should also reflect the projected symmetry of the crystal which would be fourfold in the case of [001] β-tin. However the observed zone-axis pattern only exhibited one mirror plane as shown at pole X in Fig. 2(a). It may therefore be concluded that the pattern of Fig. 1(a) is not due to β-tin.

In order to identify the unknown structure a full experimental bend-contour map was constructed and this is shown in stereographic projection in Fig. 2(a). The map exhibited two mirror planes which are marked $m$-$m$ in the figure. If we assume that SnS$_2$ losses sulphur as it decomposes but does not form β-tin, then the most likely candidate for the unknown material is SnS. This has a distorted NaCl structure and the unit cell is orthorhombic with $a=4.33$, $b=11.18$ and $c=3.98$ Å (Wyckoff, 1965). In the kinematic limit the strengths of the contours should vary with the size of the scattering factors and these were therefore computed in order to compare them with the experimental observations. Good agreement was obtained as shown in Fig. 2(b) where the widths of the lines correspond to the magnitude of the scattering factors. Diffraction patterns were also taken at the major poles and these could all be indexed in terms of the SnS structure [see, e.g., Fig. 1(d)] although variations of up to 3% in the plane spacings were observed between different specimens. This was thought to be due to non-stoichiometry caused by excess sulphur which may have remained in some of the specimens after decomposition. It should also be mentioned that although the 002 contour was observed as a strong contour and the computed electron scattering factor was large, this reflexion was not observed in the X-ray powder patterns of SnS recorded in the ASTM index.

Intermediate stages in the decomposition

After identification of the final product of the decomposition, the question remains – what is formed at intermediate stages in the process? Previously this was also explained by Günter & Oswald in terms of platelets of β-tin in a matrix of SnS$_2$ but this would appear to be unlikely if the final product of the decomposition is SnS.

A typical example of a diffraction pattern taken at an intermediate stage in the reaction is illustrated in Fig. 3(a). This shows the [001] diffraction pattern from SnS$_2$ where the hexagonal network of spots is due to the matrix. The characteristic triangles were explained by Günter & Oswald in terms of multiple diffraction from the matrix and platelets of β-tin, since the patterns may be constructed by drawing circles round each matrix spot with a radius corresponding to the 200 reflexion of β-tin. Unfortunately, there are other features of the patterns which cannot be explained by Günter & Oswald's simple interpretation. One is why...
the platelets assume a whole range of orientations with respect to the matrix and hence produce arcs rather than individual spots in the diffraction pattern. The doublets at the vertices of some of the triangles are also puzzling since these cannot be explained in terms of the 220 reflexions of \(\beta\)-tin which would only give rise to single streaks at these positions. However if platelets of SnS were present in the SnS\(_2\) matrix with (010)\(_\text{SnS}\) parallel to (001)\(_\text{SnS}_2\), then the 101 reflexions in SnS\(_2\) would produce the triangles while the 002 and 200 reflexions which have slightly different lattice spacings would give rise to the doublets as demonstrated in Fig. 3(b).

The small difference in the lengths of the \(a\) and \(c\) axes of the unit cell of SnS implies that the (101) plane is not perpendicular to the (10\(\bar{1}\)) plane. Hence there will be a certain mismatch between the SnS\(_2\) matrix and the platelets which may be responsible for the range of orientations and therefore streaking in the diffraction pattern. The orientation relation between the platelets and the matrix, namely:

\[
(010)_{\text{SnS}}/(001)_{\text{SnS}_2}
\]

has also been found by Albers & Verberkt (1970) in the SnSe system. They observed that lamellae of SnSe and SnSe\(_2\) lie with:

\[
(010)_{\text{SnSe}}/(001)_{\text{SnSe}_2} \text{ and } [101]_{\text{SnSe}}/[1\bar{1}0]_{\text{SnSe}_2}.
\]

The triangles observed in the present experiments imply that this second condition is only loosely fulfilled in the case of SnS in a matrix of SnS\(_2\).

We are currently extending the work to investigate the decomposition of SnSe\(_2\) and SnS\(_2\) and preliminary results such as those shown in Fig. 4 suggest that these behave in a similar way to SnS\(_2\). Since the lattice constant is \(a=3.645\) Å in SnS\(_2\) and \(a=3.807\) Å in SnSe\(_2\) (Rimington, Balchin & Tanner, 1972), the spacing of the matrix diffraction spots will be different for the two materials. If platelets of \(\beta\)-tin were present in either material the radii of their diffraction circles centered on the matrix spots would be the same but their overlap would be different. Hence the relative sizes of the triangles could change markedly from SnS\(_2\) to SnSe\(_2\). However if the circles were produced by the 101 reflexion in SnS or SnSe respectively, the (101) plane spacing also changes by \(\sim 3\%\) from SnS to SnSe (Wyckoff, 1965). Hence the increase in the plane spacing of the matrix would be similar to the increase in plane spacing of the platelets. The two effects should then cancel leaving triangles of a similar size in the two cases as shown in Figs. 3 and 4.

This investigation has illustrated both the dangers of the isolated use of selected-area diffraction and the usefulness of the real-space techniques. We are now attempting to go one stage further in the analysis by simulating the bend contours in these materials and propose to report detailed observations of the decom-

Fig. 3. (a) [001] diffraction pattern at an intermediate stage in the decomposition of SnS\(_2\). (b) Constructed pattern in terms of platelets of SnS in an SnS\(_2\) matrix.
position of SnSSe and SnSe₂ along with contour simulations in a future paper.

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References


Fig. 4. The patterns corresponding to Fig. 3(a) for (a) SnSSe and (b) SnSe₂.