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Atomic String Potentials and the Form of [0001] Zone Axis Patterns of GaS, GaSe and InSe

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Abstract . — The relationship between the form of hexagonal zone axis patterns and the projected atomic potential is explored as a method for polytype identification of GaS, GaSe and InSe. As the various known polytypes of these materials project to give unit cells with very different simple-string potentials this relationship may be exploited by making use of previous related work. It is found that this method is simple to apply and consistent with the results of more conventional analyses based on the symmetry of convergent beam electron diffraction patterns. Growth faults could, however, cause ambiguities in the method of analysis.

1. Introduction

It is interesting to review the [0001] large angle convergent beam electron diffraction (LACBED) zone axis patterns of De Blasi and co-workers published for GaS, GaSe and InSe [1-4] in terms of the string potential concept. No doubt this is an activity that would have occupied his attentions in due course had circumstances been otherwise.

The idea of atomic string potentials is a natural consequence of the projection approximation that is often made in the case of diffraction of energetic particles by crystal lattices. It is widely used in channeling studies by high energy physicists [5] and it has proved extremely useful in high energy electron diffraction [6, 7] following on from the work of Berry [8], Buxton [9] and Bird [10]. One simply projects the crystal structure of interest along the direction of incidence. Lines of atoms aligned along zone axes produce cylindrically symmetric potential wells. Electron states in the crystal are either bound in a specific sub-set of wells or are free to wander from one well to another. Both wave and particle concepts may be used to analyse the electron diffraction that occurs (Berry [11]). This approach allows one to categorize diffraction problems according to the real-space arrangement and strength of atomic strings. In favorable cases it leads to straightforward analysis of the elaborate and often very beautiful forms of electron diffraction zone axis patterns. We here study the application of this approach to the published work of De Blasi and his co-workers.

2. The Projected Potentials of GaS, GaSe and InSe

The form of zone axes that project with hexagonal symmetry and have projected potentials that can be formed from cylindrically symmetric atomic strings of various strengths has been quite thoroughly studied in the past [12, 13]. According to the work of De Blasi *et al.* [1-4], and the references cited therein, the various common forms of GaS, GaSe and InSe project into three versions of the three-string case, as illustrated in Figure 1. In the notation of De Blasi *et al.* [1-4] the β -2H form, typical of GaS, generates a projected potential that is composed of two identical atomic strings in the A position. The ϵ -2H and δ -4H forms of GaSe project with a (Ga + Se) string in the A position, a Ga string in the B position and a Se string in the C position. The γ -3R form of GaSe projects as a simple string case with identical (Ga + Se) strings in each of the A, B and C positions. Projected potentials of these types are similar to those formed by the various polytypes of transition metal chalcogenides and we will examine the zone axis patterns of De Blasi and co-workers in relation to the earlier work on these more widely studied compounds.

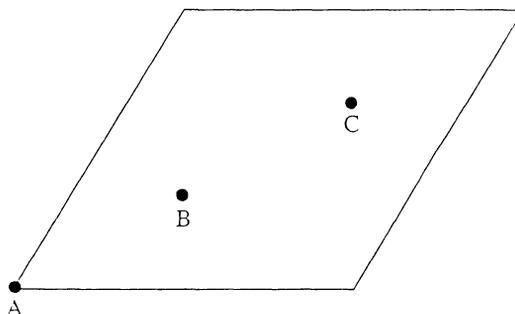


Fig. 1. — Schematic form of hexagonal projected potentials with three possible positions, A, B and C, for the location of atomic strings.

3. Examination of Experimental Results

3.1 β -2HGaS — The [0001] projection of the β -2H form of GaS gives rise to a projected potential of the same form as that of the 2H_b polytypes MoS₂, MoSe₂ and WSe₂. The strength of the atomic strings of GaS is given to a first approximation by $\frac{(Z_{\text{Ga}} + Z_{\text{S}})}{c} \frac{a^2}{3\sqrt{3}}$ while that of the transition metal (TM) chalcogenides (C) is given by $\frac{(Z_{\text{TM}} + 2Z_{\text{c}})}{c} \frac{a^2}{3\sqrt{3}}$ [7]. In these expressions Z_{A} is the atomic number of the element A, and a and c are the unit cell lattice constants. From these expressions we find that the string strength parameter for GaS (15.0) lies between that of MoS₂ (11.6) and MoSe₂ (17.7). It is therefore interesting to compare the results of De Blasi *et al.* with those of MoS₂ and MoSe₂, all recorded at a microscope operating voltage of 120 kV (Fig. 2). In fact the details of these patterns have been shown to depend very strongly on the specimen thickness and the microscope operating voltage [14] so that an exact match would be very difficult to achieve. Nevertheless, the similarity of the three patterns in Figure 2 is evident and close study,

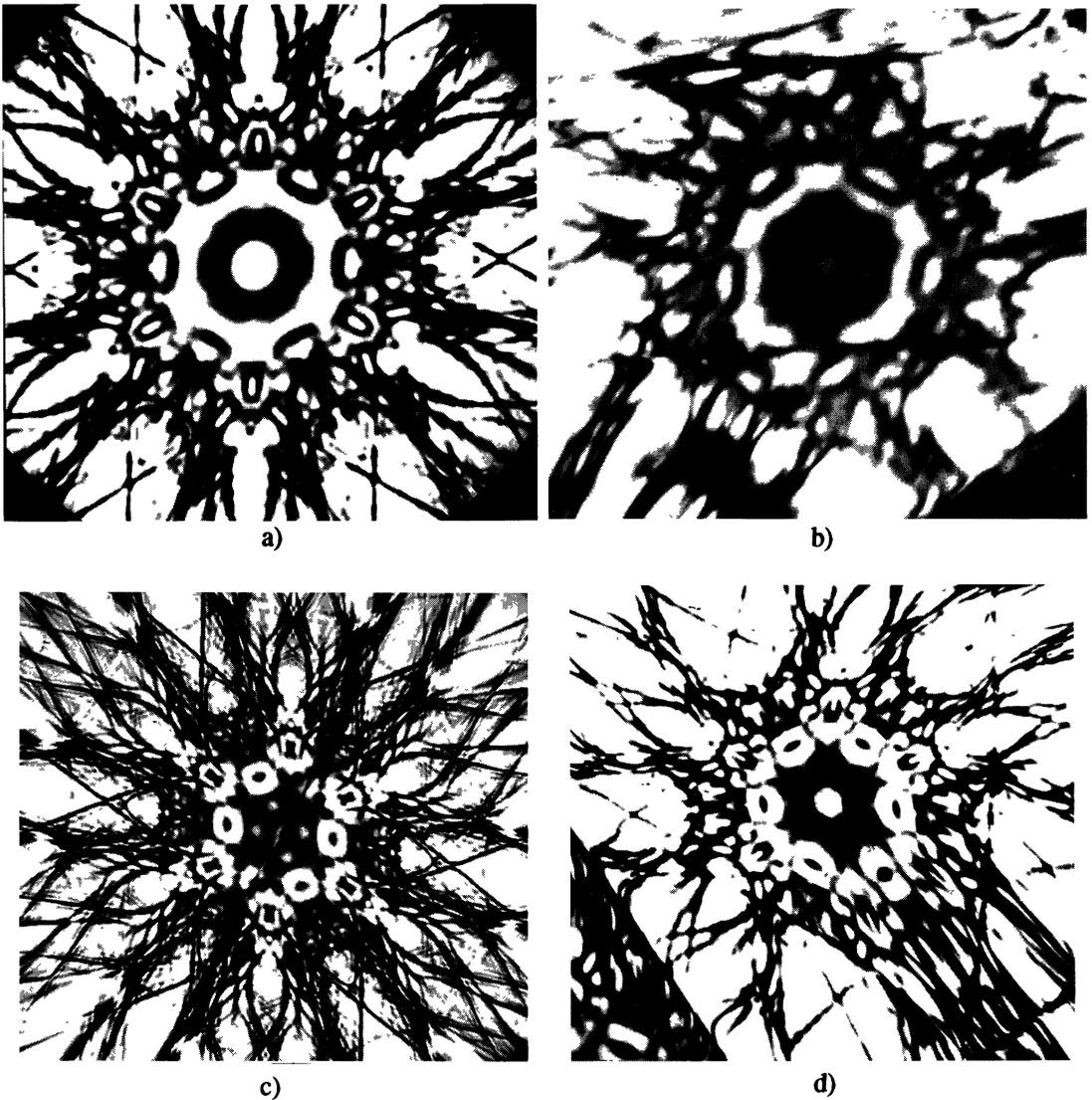


Fig. 2. — a) [0001] LACBED pattern of β -2H GaS (Fig. 2c of [1]) to be compared with b) a [0001] bend contour pattern of MoS_2 c) a further [0001] LACBED pattern of β -2H GaS (Fig. 1 of [3]) for a different film thickness (with a dislocation crossing the centre of the pattern) compared with d) a [0001] bend contour pattern of MoS_2 . All patterns were recorded at a microscope operating voltage of 120 kV.

involving patterns obtained at different specimen thicknesses and operating voltages, indicates that the GaS result is closer to those of MoSe_2 than MoS_2 .

3.2 3R GaSe and InSe — According to the work of Steeds *et al.* [7] these simple-string zone axes have string strengths given approximately by $\frac{2(Z_{\text{Ga}} + Z_{\text{Se}})}{c} \frac{a^2}{3\sqrt{3}} \approx 14.3$ and $\frac{2(Z_{\text{In}} + Z_{\text{Se}})}{c} \frac{a^2}{3\sqrt{3}} \approx 20.5$

These values put the 3R GaSe zone axis between the $\langle 111 \rangle$ zone axis of Si, which has a string strength of 12.7, and that of Ag $\langle 111 \rangle$ which has a string strength of 16.0. InSe lies between the values for Ag $\langle 111 \rangle$ and Au $\langle 111 \rangle$, with a string strength of 27.1, and Ge $\langle 111 \rangle$ with a string strength of 30.2. The patterns that they show (for example, Fig. 1 of [2]) are hence very similar to previously published results for simpler materials [6, 13] except those for Si $\langle 111 \rangle$ where the absorption is considerably lower so that ring patterns dominate the centre of the silicon patterns but are extinguished in the cases of GaSe and InSe and also for Ag, Ge and Au $\langle 111 \rangle$ patterns.

3.3 ϵ -2H GaSe — This case is rather similar but somewhat different from others that have been studied previously [12] because each of the three strings is of different strength. However, since the atomic number difference between Ga and Se is rather small (31 and 34 respectively) we can expect strong similarities to the cases when the B and C string strengths are identical. The A strings, by way of comparison, are much stronger and depend on $(Z_{\text{Ga}} + Z_{\text{Se}})$. As a result, we conclude that the projected potential is rather similar to that of 2H TaSe₂ in that the A atomic strings are approximately twice as strong as the B and C strings. This conclusion is consistent with a comparison (Fig. 3) between the published results for ϵ -GaSe and previously unpublished results for 2H TaSe₂ (but see [12] for other related zone axis patterns).

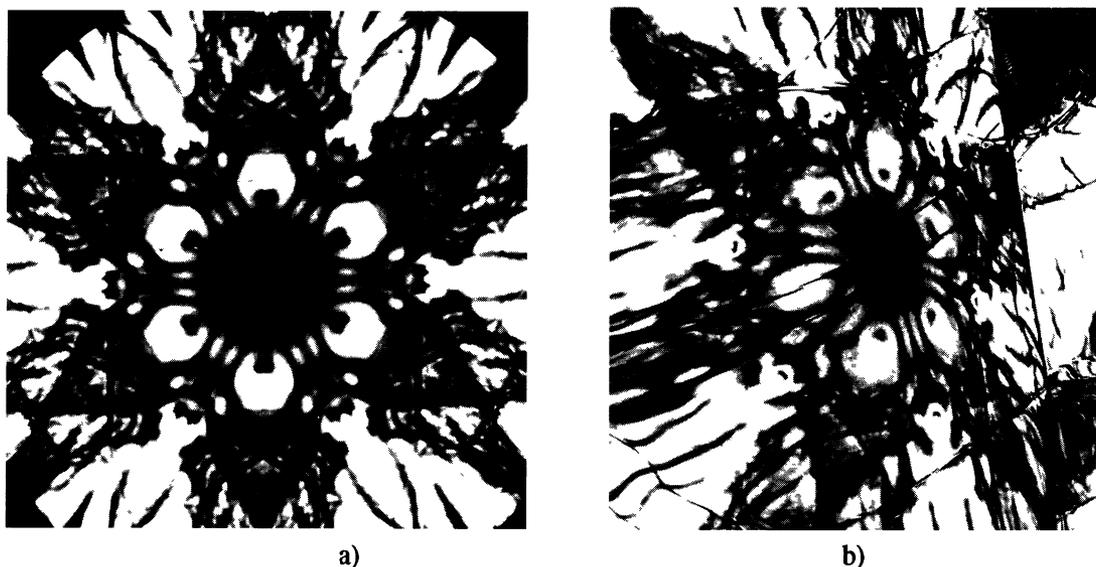


Fig. 3. — a) [0001] LACBED pattern of ϵ -2H GaSe (Fig. 2a of [1]) compared with b) a [0001] bend contour patterns of 2H TaSe₂ both taken at 120 kV.

4. Discussion

The work of De Blasi [1-4] and co-workers in identifying polytypes of GaS, GaSe and InSe has been confirmed by a completely independent method of analyzing their results. The wealth of detail present in zone axis patterns and the eye's ability at pattern recognition makes it a relatively simple matter to compare experimental results obtained from unknown polytypes with previously

published results. The classification of zone axis patterns with hexagonal symmetry follows a well-established route, depending on the number of independent atoms strings per projected unit cell and their strengths, defined here by a simple formula. It should however be pointed out that a more precise definition of atomic string strength is given elsewhere [7] and should be used in cases where detailed examination is required. In the case of the zone axis patterns studied here the differences were so great and the similarities to existing results in the literature so strong that the more accurate determination of string strengths was unnecessary.

Of course this method used for polytype identification has its limitations. As the results depend on projected structure, stacking disorder may not be immediately apparent and the patterns from disordered materials could give misleading results. For example, typical disorder could lead to slabs of ordered material displaced so that A positions in the projected unit cell are translated to B or C positions of adjoining slabs. Often when this occurs the result is a lowering of the zone axis pattern symmetry from 6 mm (typically to 3 m or m symmetry). However, such symmetry breaking may not be apparent without taking recourse to the more sensitive techniques of symmetry determination by convergent beam electron diffraction exploited by De Blasi and his associates.

However, zone axis patterns from defect free polytypes do have the advantage that they may be used to determine the nature of the projected charge distribution. Either by zone axis critical voltage measurements [12] or by the extension of methods currently in use on Si, Ge and diamond [15, 16] accurate structure factor information can be obtained by well worked-out procedures. The structure factors may then be used to determine the charge distributions. By use of energy filtering of the results and attention to a number of practical details, very accurate results are now being achieved this way.

5. Summary and Conclusions

It has been demonstrated that the atomic string potential concept can be applied to the problem of identification of the polytypes of GaS, GaSe and InSe previously identified by other methods by De Blasi and his associates [1-4]. This method makes use of information present in large angle convergent beam electron diffraction results that are generated very simply in the course of investigation of materials by electron diffraction. It is limited to zone axes that project in the form of a relatively small number of independent atomic strings and to defect free regions of the material under study.

Acknowledgements

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