Observation of Polytype Stacking in Tetrahedral Compounds

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Polytype stacking is observed directly in CuAsSe, a typical tetrahedral compound, in high resolution electron images taken with a commercially available 200 kV electron microscope.

The structure of CuAsSe[1] is related to the wurtzite 6H structure of ZnS, but in CuAsSe both sites of the 6H structure are occupied in an ordered manner by Cu, As, and Se (Figure 1). The stacking of layers up the long *c*-axis of this material may be expressed as 3,3 or as hcc stacking.

We now report that by suitable thermal treatment or by partial substitution with S and Ge, a whole range of polytypes can be produced. Single crystals of two of these polytypes with 4,4 (hccc) and 3,4 (hcchccc) stacking have been obtained in sufficient size for *X*-ray single crystal study. We have found conditions under which polytype stacking may be inferred directly from high resolution lattice images obtained in a JEOL 200 CX electron microscope used in top-entry configuration with an ultra-high resolution pole piece, double-gap condenser, and using a LaB_6 electron source. We have observed numerous polytypes of CuAsSe and observed intergrowths between polytypes. The interpretation has been substantiated with quantitative calculations.

Figure 2 shows a micrograph (taken at a magnification of 730 000) of a wedge-shaped crystal of CuAsSe. The stacking sequence of polytypes is indicated, with the alternation of successive runs of diamond-like and wurtzite-like stacking being immediately apparent. Figure 3 is an enlargement of a portion of the 3,3 polytype lattice image of Figure 2 with a

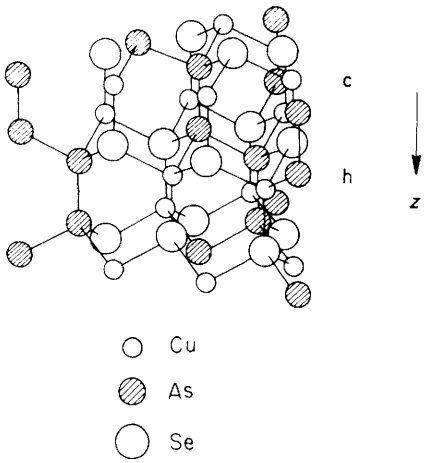

Figure 1. A perspective view along the *a*-axis of 3,3 CuAsSe showing successive hexagonal and cubic stacked layers of the structure.

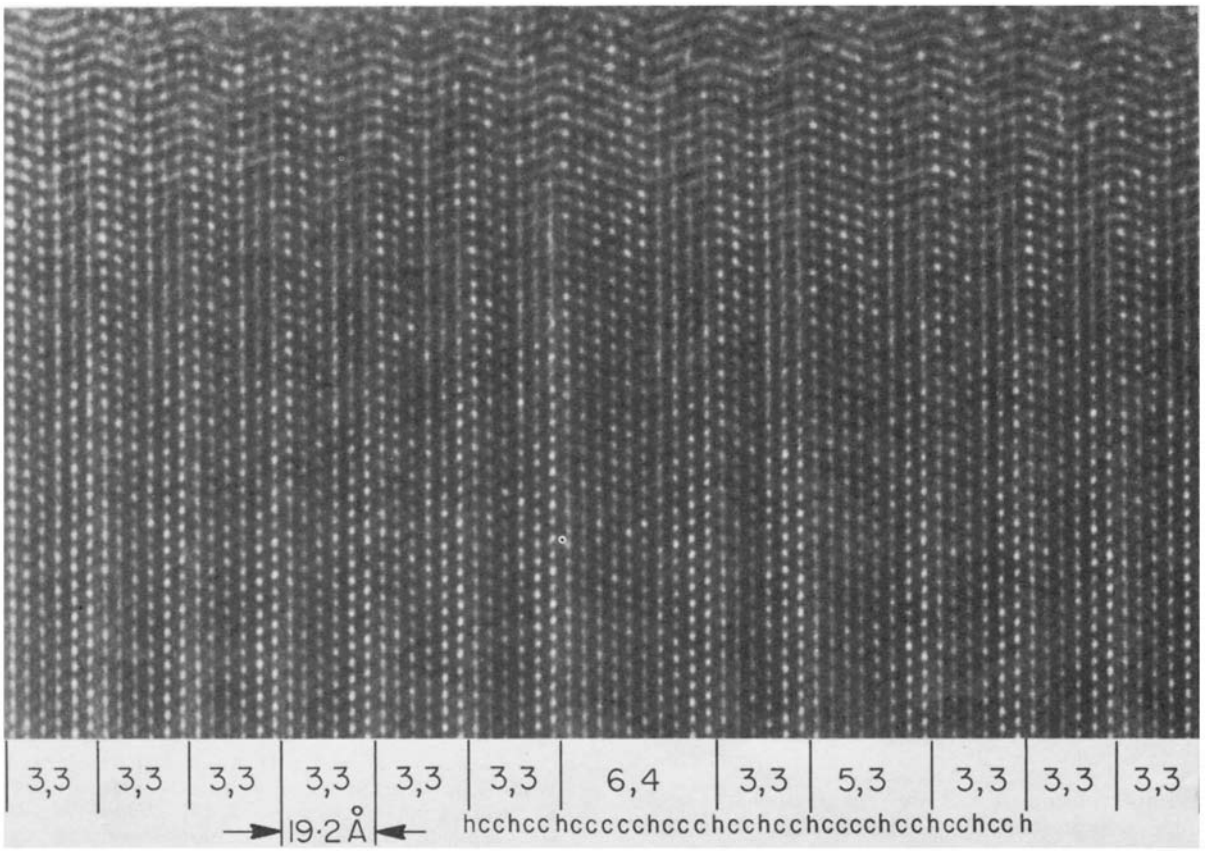

Figure 2. Lattice image of 3,3 (hcc) pseudo-6H polytype of CuAsSe (a = 11.75, b = 6.79, c = 19.21 Å) viewed down its *a*-axis with 200 kV electrons.

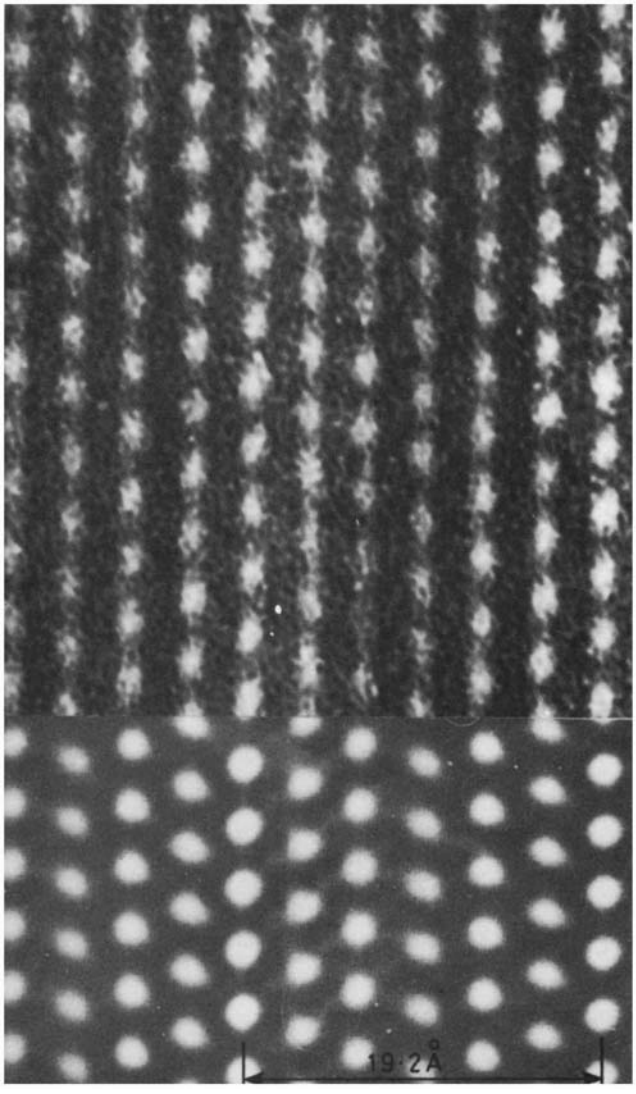

Figure 3. Enlargement of a portion of lattice image of Figure 2 with, below it, a comparison calculated lattice image, using a C_s (= coefficient of spherical aberration) of 0.95 mm and a defect of focus −1000 Å for a 188 Å thick crystal of 3,3 polytype of CuAsSe.

calculated image of that polytype for comparison. The incident electron beam is tilted at an angle of 0.003 radian from the *a*-axis towards the 011 direction of the crystal in the calculated image and this makes the superlattice period more apparent in accord with the observed lattice images.

CuAsSe is typical of a whole range of binary, ternary, *etc.* compounds with tetrahedral structures related to the sphalerite and wurtzite types. The immediate elucidation of stacking faults in the whole class of materials is now possible with a commercially available 200 kV electron microscope.

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References

1 H. J. Whitfield, *J. Solid State Chem.*, 1981, **39**, 209.