NOTES AND NEWS

A MODIFIED HULL-DAVEY CHART FOR HIGH VALUES OF *c/a*

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In the course of recent syntheses of iron oxides (Holser and Schneer, 1953) and an investigation of polymorphism in one dimension (Schneer, 1953), the routine identification of multi-layer polymorphs in powder photographs became necessary. Published charts of the Hull-Davey (1921) type extend only to *c/a* (5.4), (Fairbanks, 1928, or Davey, 1934).[1] A new chart, Fig. 1, was constructed for trigonal and hexagonal spacings covering *c/a* ratios from 3 to 18, corresponding to unit cell heights in close-packed structures of 4 to 21 layers. After the method of Owen and Preston (1923; *Cf.* Ewald, 1923; Harrington, 1938), ordinates were plotted on a logarithmic scale. The curves were plotted from approximately 1,000 spacings. Lines for (*hhl*), *l* not divisible by 3 or 2, were omitted. The omitted spacings occur only if there are no glide planes as in Davey's (1934) "simple triangular lattice." This symmetry occurs in close-packed structures only for randomly stacked layers, in which event there is only one layer per unit cell and the previously published charts may be used. Non-close-packed structures with random layer stacking are not likely to exceed the limit of Davey's chart.

Bravais-Miller indices (*hkil*) with *i* omitted are employed throughout.

USE OF THE CHART

Recapitulating Hull and Davey (1921), a strip of paper is placed along the horizontal scale. The *d* spacings of the unknown, as determined from a powder photograph, are marked on the strip against the scale. If the composition of the mineral is known and the structure is close-packed, the (100) spacing equals $\sqrt{3}\times$(anion radius). The strip is placed with this spacing on the vertical (100) line of the chart, and moved vertically over the chart until all of the marks on the strip simultaneously intersect lines on the chart. Indices and *c/a* are read directly. If the layer height of a unit cell is within the range 4 to 21 and the structure is close-packed, the marks should meet lines at an integral layer height. If the (100) spacing is not known in advance, the strip must be slid back and forth horizontally as well as vertically in search of a match position.

Because of the characteristic syntaxic intergrowth of layer poly-

[1] An unpublished chart by A. E. Austin, Battelle Memorial Institute, extends to *c/a* (10), and a chart by R. E. Riley and W. Rostocker, Armour Foundation, extends to *c/a* (2.7).

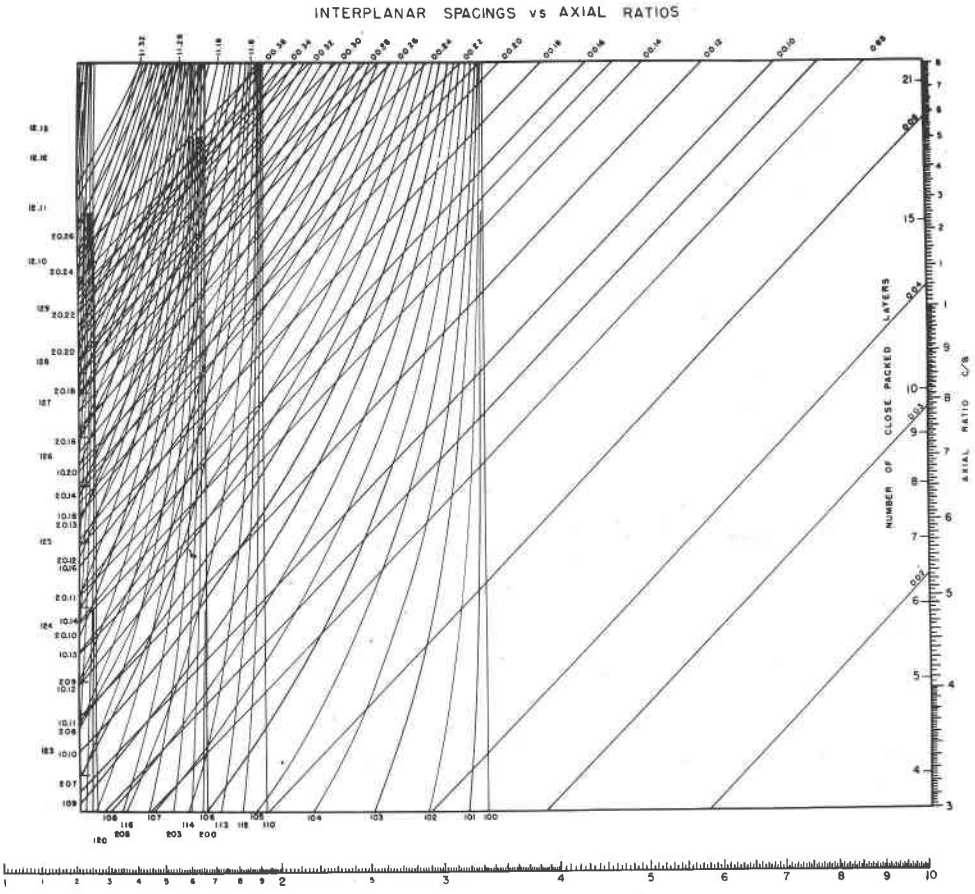

FIG. 1. Chart for high values of c/a.

morphs (Mitchell, 1953) and the increase in the density of lines with increase in the number of layers, a powder photograph of a syntaxic intergrowth of small layer height polymorphs might be difficult to interpret. The characteristic close-in lines of high spacings are lost in the central blind region of the Straumanis film. For these reasons, the chart is chiefly useful in detecting polymorphic changes in the course of thermal treatment of powder samples. Like the powder method itself, results may be statistical, with all of the advantages and disadvantages that go with an averaging procedure.

EXAMPLES

Figure 2 illustrates data from three separate powder patterns, representing three compounds which are chemically distinct but struc-

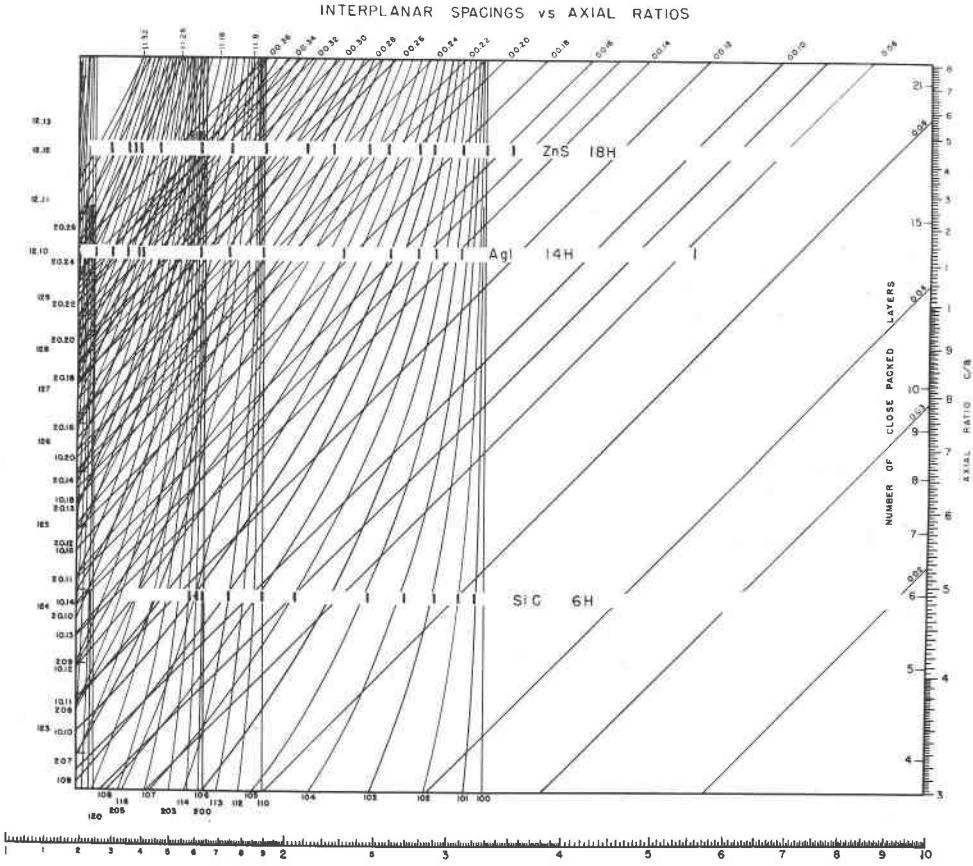

FIG. 2. Examples. Plots of observed spacings from powder photographs of SiC (6H) after Thibault, ZnS (18H?), and AgI (14H?).

turally uniform. The lower strip is SiC (6H). Spacings are as observed by Thibault (1944). The graph was constructed primarily to identify spacings in multi-layer polymorphs in a series of experiments now in progress on the thermodynamics of polymorphism in one dimension. Multilayer polymorphs are interpreted as intermediate stages in the course of second order transformations of the sphalerite-wurtzite type (Schneer, 1955). The upper strip of spacings are from the diffraction pattern of ZnS sublimate at 600° C. While the pattern is incomplete, the lowest position on the graph at which coincidence of lines may be obtained is at c/a 14.720, which is the ratio for ideally packed layers of an 18 layer polymorph. The central strip, even less complete, nevertheless contains lines which can be matched first at c/a 11.445 which is

the ratio for ideally packed layers of a 14 layer polymorph. The compound represented by the central strip is AgI held for 24 hours at 120° C. and quenched to room temperature. The experimental work referred to above is now centered on AgI as offering a weakened model structure on which to test the theory of polymorphism in one dimension. Experiment to date has indicated that thermally treated powders yield faint but unmistakable lines on powder diffraction photographs in addition to those identifiable as characteristic of the sphalerite and wurtzite structures. These lines may be indexed graphically as illustrated above. The occurrence of one dimensional polymorphism or *polytypy* in AgI was anticipated by the theory.

ACKNOWLEDGMENTS

The graph was begun at the suggestion of Dr. William T. Holser whose encouragment and assistance are reflected throughout this paper. Some of the computations were paid for by the Office of Naval Research. Mr. John Pollock of the University of New Hampshire Engineering Experiment Station, traced the graph. Mr. Auguste Planchon, of the University of New Hampshire, assisted with the AgI research. R. C. Lesser of the Cornell Computing Center, Cornell University, supplied the majority of the computations.

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