APPLICATION OF THE LAUE PHOTOGRAPH TO THE STUDY OF POLYTYPISM AND SYNTAXIC COALESCENCE IN SILICON CARBIDE*†

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ABSTRACT

The purpose of this paper is to give a summary of the relationships between Laue photographs of various polytypic forms of silicon carbide. A knowledge of these relationships makes this method readily applicable to the (*a*) discovery of new polymorphs, (*b*) determination of syntaxic intergrowths and coalescence and, (*c*) identification of many-layered rhombohedral types.

The use of the optical goniometer in the study of polytypic substances as well as their syntaxic coalescence and intergrowths was greatly emphasized by Thibault (1944). The importance of the optical goniometer must still be emphasized, but recently, especially with the discovery of rhombohedral silicon carbide types with a large number of layers, its limitations are more clearly seen. In this laboratory, for example, crystals that showed blurred faces in the goniometer were usually discarded. Later it was learned that a great number of these are rhombohedral modifications of many layers. These could only be identified with the use of the Laue methods which will be described. Now that this fact is known, it is possible to sort out, for x-ray investigation, those crystals that have possibilities of being new modifications. With our present knowledge of the polymorphs of silicon carbide, coalescence and syntaxic intergrowths are now more easily perceived and identified by x-ray methods than by the optical goniometer.

THE INTERPRETATION OF SILICON CARBIDE LAUE PHOTOGRAPHS

Because type $6H$ is the most common polymorph of silicon carbide it will be used in the following discussion which is aimed at showing some geometrical relationships between the crystal faces, reciprocal lattices and Laue photographs of this substance.

In Fig. 1 lines AE, AF, AG, AH and AI represent the slopes of the $6H$ $10\cdot l$ faces as indicated. Lines AR_1, AR_2, AR_3, AR_4 and AR_5 are perpendicular to AE, AF, AG, AH and AI, respectively. The intersections of these AR_n lines with the gnomonic plane, represented by BR_1, give the gnomonic projection of the $10\cdot l$ faces (G_n). The intersections of the AR_n lines with DR_6 establish a reciprocal lattice network of these $10\cdot l$ faces. The distance between each of these is equal to DR_1. In

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this discussion we are concerned with the planes in the range D to R_6. Point R_6 was not established by the use of an external face since this face is not present on the crystals, but it must be used because we are considering a 6 layer form. The distance DR_6 represents the reciprocal

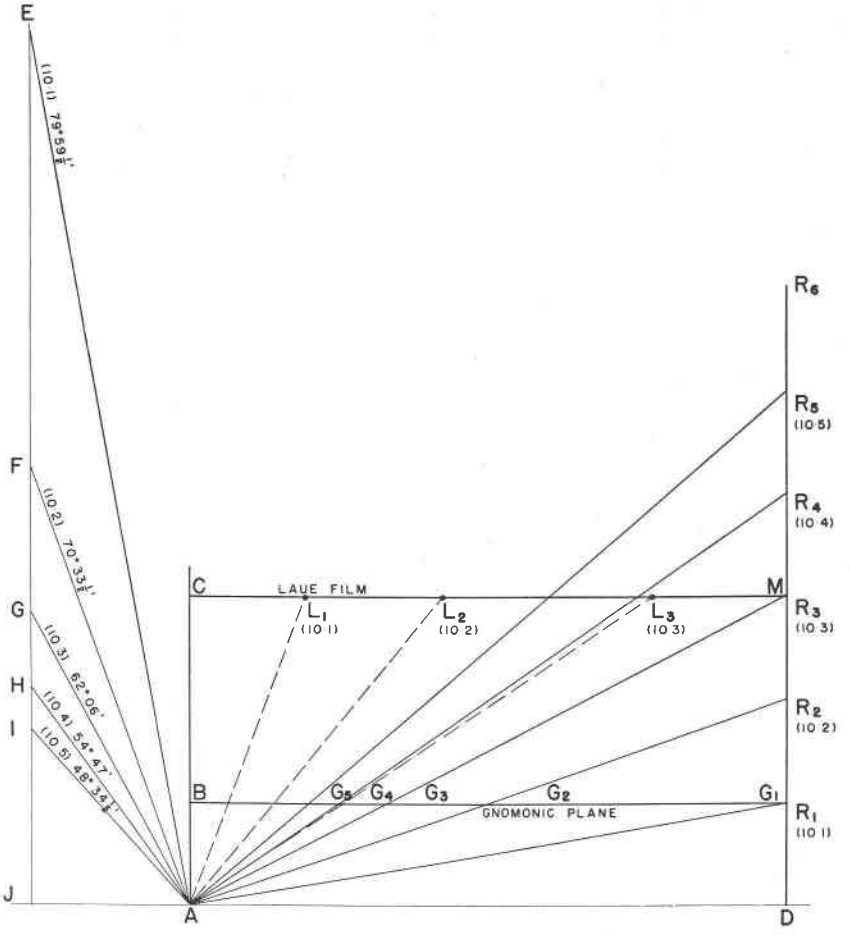

FIG. 1. Some geometrical relationships between the crystal faces, reciprocal lattice, gnomonic projection and Laue photograph of silicon carbide type 6*H*.

distance of one layer of the structure. This single layer of $d=2.513$ kX* is the basic unit in all silicon carbide forms. Line CM represents a flat Laue film. The L_n points represent the Laue spots of the $10 \cdot l$ reflections.

* This dimension is given in kX units to agree with the previously published values for the various SiC types.

TABLE 1

n	DR_n (cm.)	CL_n (cm.)
1	.2	.21
2	.4	.42
3	.6	.64
4	.8	.85
5	1.0	1.07
6	1.2	1.29
7	1.4	1.51
8	1.6	1.73
9	1.8	1.95
10	2.0	2.19
11	2.2	2.42
12	2.4	2.66
13	2.6	2.91
14	2.8	3.16
15	3.0	3.42
16	3.2	3.68
17	3.4	3.96
18	3.6	4.24
19	3.8	4.53
20	4.0	4.84
21	4.2	5.15
22	4.4	5.49
23	4.6	5.83
24	4.8	6.19
25	5.0	6.57
26	5.2	6.97
27	5.4	7.40
28	5.6	7.84
29	5.8	8.32
30	6.0	8.83
31	6.2	9.37
32	6.4	9.95
33	6.6	10.58
34	6.8	11.25
35	7.0	11.99
36	7.2	12.78
37	7.4	13.66
38	7.6	14.62
39	7.8	15.70
40	8.0	16.88

The R_n points are related to the L_n points according to the equation $\angle CAL_n = 2\angle DAR_n$ (1). It is, therefore, easy to determine the positions of the $10 \cdot l$ spots on a Laue film if the R_n points are known.

It was stated above that the distance DR_6 is the reciprocal of the basic

unit, 2.513 kX, of all silicon carbide forms. Because this is a reciprocal relationship it follows that this distance can be divided into as many spaces as there are layers in the structure built up of this basic unit. We saw above that this distance in the 6*H* modification was divided into 6 parts. In 8*H*, 10*H* and 19*H* the distance DR_6 would be divided into 8, 10 and 19 spaces, and in these cases R_6 would become $10\cdot 8$, $10\cdot 10$ and $10\cdot 19$, respectively. Using equation (1) one can easily see from this discussion how the positions of the $10\cdot l$ spots (L_n) can be predicted on a Laue film from the known R_n positions of any form of silicon carbide. The rhombohedral forms can be predicted in the same manner as long as one remembers that the $10\cdot l$ reflections are missing when $-1+l\neq 3n$.

To facilitate the construction of Laue patterns of silicon carbide with a crystal to film distance of 6 cm., DR_6 was made equal to 12 cm. This distance was then arbitrarily divided into 60 R_n spaces and the corresponding L_n positions were determined by the formula $L_n=6\tan 2\angle DAR_n$. It was only necessary to calculate the first 40 L_n positions because the flat Laue film is seldom large enough to register more than this. The relationships are summarized in Table 1. These CL_n distances are plotted in scale form in Fig. 2, where each line is one of the 40 L_n positions. Each of these positions on the Laue film represents a corresponding reciprocal lattice R_n position. Therefore, on the scale, these have been labelled in centimeters according to the DR_n spacings as shown in Table 1. With the use of this scale one only has to think about the DR_n spacings. In order to show by example how this scale is applied, the positions of the $10\cdot l$ Laue spots will be determined for the hexagonal form 19*H*. Dividing 12 cm. (DR_6), by 19, the number of layers in the modification, gives the value 0.63 cm. This distance marked off on the scale (Fig. 2) gives the

FIG. 2. Scale for the construction of silicon carbide Laue patterns with a crystal-to-film distance of 6 cm. (The scale has been reduced one-half.)

position of the first 19*H* $10\cdot l$ reflection, $10\cdot 1$. Multiples of this distance give the other $10\cdot l$ spots. The $10\cdot \bar{l}$ reflections are in the same positions on the opposite side of the origin. The procedure for the rhombohedral type 33*R* is the same. Twelve divided by 33 gives 0.363 cm. This distance on the scale gives $10\cdot 1$. Twice this distance in the opposite direction gives $10\cdot \bar{2}$. The other spots, both negative and positive, fall on equally spaced points at 3 times 0.363 cm.

The writer has calculated the spot positions for numerous postulated as well as known forms of silicon carbide, and has arranged the results

in two charts, one of the hexagonal modifications and one of the rhombohedral modifications. This latter chart is reproduced in Fig. 3.* If the chart is made to the same scale as the Laue crystal-to-film distance it is a relatively easy matter to slide the center of the film down the 0 line and find the corresponding spot positions, thus identifying the silicon

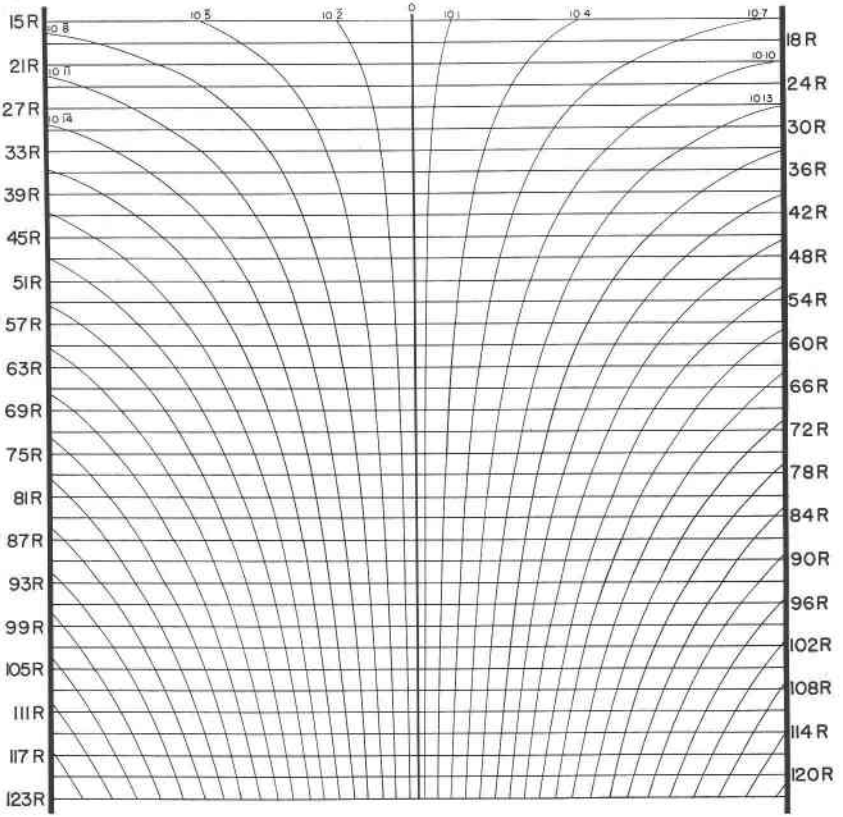

FIG. 3. Chart for the rapid identification of rhombohedral silicon carbide types from Laue films.

carbide modification or modifications. One must, however, be aware of the fact that the $10 \cdot l$ spots are not the only ones present on the film. More often than not, especially in types consisting of a few layers, other spots appear in the midpoints between the $10 \cdot l$ spots, as well as at other odd positions. Only those at the midpositions give trouble because they frequently give the impression that the crystal form has twice as many

* A number of the forms on this chart are theoretically impossible, but were included in order to give continuity to the chart.

layers to the unit cell than it actually has. This ambiguity is easily eliminated by further investigation with the rotating crystal methods. With a little experience one is not hindered greatly with the presence of these "unwanted spots." In a number of the many-layered rhombohedral modifications investigated in this laboratory, these have been much weaker than the $10 \cdot l$ spots or absent altogether.

Syntaxic coalescence is very common in silicon carbide. The effect of this property on the x-ray films is a superimposition of the patterns of each of the types. It is usually a very simple matter to differentiate between these superimposed patterns. This is true because the coalescence in nearly every case investigated consists of not more than three modifications and in these, two of the types were either $6H$, $15R$ or $4H$. Standard films of these should be available to make identification easier, but in case they are not available, one can determine the spots on the basis of the Laue pattern constructions described above. Actually, the coalescence of a common type in an unknown crystal is often helpful since the known spots are valuable reference points in determining the unknown form.

The Advantages and Limitations of the Laue Method

The Laue method has a great advantage over most of the x-ray techniques when it comes to the many-layered rhombohedral forms, in that it resolves the spots much more than in these other conventional methods. Figure 4 shows the relative resolution of the $10 \cdot l$ reflections by three conventional x-ray methods, using CuK_α radiation. The crystal-to-film distance was 6 cm. for both the Laue and precession films, and the Weissenberg camera had a diameter of 5.73 cm. The over-all figure has been reduced in size. This greater resolving power of the Laue method has been used to advantage by other writers. Honjo, Miyake and Tomita (1950) were enabled, by observations taken from cylindrical Laue photographs, to identify their $594R$ silicon carbide. Ramsdell and Kohn (1952) also used Laue photographs to give sufficient resolution for the positive identity of their $84R$ polymorph. The recent positive identification of types $141R$, $168R$, and $192R$ at this laboratory was based upon Laue films.

Another important advantage of the Laue method is the speed at which one can prepare the crystal and take the photograph. Since the pictures are taken with the c axis parallel to the x-ray beam, it is a simple matter to orient them. Excellent basal pinacoids are nearly always present on crystals of this substance. The writer has observed many crystals which possess no other faces but the basal pinacoid. Using the Laue method these can be identified.

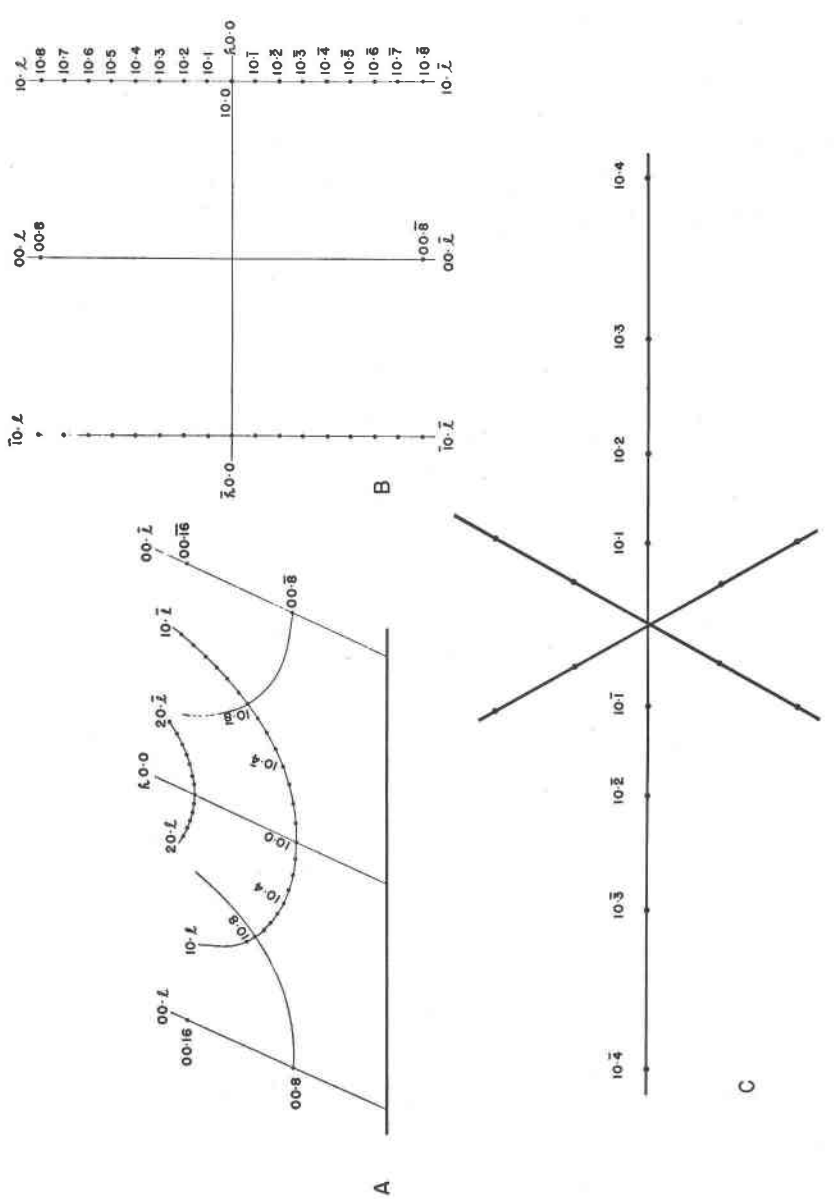

FIG. 4. The relative resolution of $10 \cdot l$ reflections for silicon carbide type $8H$ by the Weissenberg method (A), Buerger precession method (B) and Laue method (C). Crystal-to-film distance, 6 cm. for Laue and precession films, Weissenberg camera diameter, 5.73 cm.; CuK_α radiation. The over-all figure has been reduced in size.

This method has three disadvantages. Two of these, which have been mentioned above, are not serious. These are the presence of "unwanted" spots, and the limited number of $10 \cdot l$ spots that appear on the regular size flat film. The third disadvantage has to do with the intensities of the spots. One is usually not concerned with this, however, unless he has found a new type and desires to calculate its structure. In this case he can investigate the crystal further using an a axis Weissenberg film or a Buerger precession film showing a^* and c^*.

The writer has not investigated any other polytypic compound but he feels that the principles considered in this paper could easily be applied to other substances of this same nature. It might be mentioned that Frondel and Palache (1950) have published Laue patterns of the zinc sulfide types $4H$, $6H$ and $15R$ and have stated that the forms can be separated conveniently by direct comparison of these films.

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