The determinantal equation for the continuity condition may be set up in the usual way and reduced to[15]

$$\tan^2 \pi u = -\frac{2\delta(1+1/2^{\frac{1}{2}}\varphi')+(\varphi-\pi)2\times 2^{\frac{1}{2}}/\varphi'}{(\pi+\varphi/2^{\frac{1}{2}}\varphi')(1+\delta/\sigma)}. \quad (15)$$

This is to be compared with the equation

$$\tan^2 \pi u = -2\delta/\pi(\delta/\sigma+1), \quad (16)$$

which is obtained in the absence of tangential boundary conditions. Due to smallness $1/\varphi'$, π/φ' and φ/φ' for energies in the first zone, the new expression is equivalent to the old. In the second zone, however, the results, shown in Fig. 4, using the first f function ($\varphi' = -21\times 2^{\frac{1}{2}}$) are actually worse than the old. From a suitable linear combination of the two f functions any desired value of φ' can be obtained. The arbitrarily chosen value 10.8 gives the curve which fits the correct parabola fairly well.

VII. CONCLUSIONS

The results of the cellular method of finding wave functions are probably quite good for the occupied states of the metals so far calculated. For excited states, however, very large errors are to be expected. This cannot be overcome by such simple expedients as adding a few more joining conditions to those already in effect. It appears that the number of new conditions necessary to take care of higher energies would make the labor of calculation prohibitively difficult. However, a new method of attack has been proposed by Slater and it is to be hoped that it will circumvent these difficulties.

Finally it should be remarked that this work has been concerned with only one aspect of the electronic theory of solids. Although accurate solutions of the wave equation in the crystal would be very valuable they suppose that each electron sees a static potential field in which the influence of the other electrons is represented by an average. Actually relative positions of the electrons, correlation effects, must be considered in order to explain many properties, for example the binding energy of the alkali metals[16] and the phenomenon of excitation in insulators.[17]

The writer would like to express his gratitude to Professor Slater, under whose direction work on this problem was commenced, and whose continued interest has been instrumental in its completion.

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[15] The reader is referred to references 2, 5 and 6 for the general method of setting up the determinantal equations of the cellular method.

[16] E. Wigner, Phys. Rev. **46**, 1002 (1934).

[17] J. C. Slater and W. Shockley, Phys. Rev. **50**, 705 (1936).

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Theory of the Use of More Than Two Successive X-Ray Crystal Reflections to Obtain Increased Resolving Power

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If an x-ray beam is selectively reflected from more than two crystal surfaces in succession it is shown in this paper by a simple method of graphical analysis that it should be possible to obtain resolving power considerably superior to the best obtainable with present two crystal x-ray spectrometers. This extension and generalization of the two crystal spectrometer principle in one of its forms (the three crystal spectrometer) should permit the study of the asymmetric diffraction patterns predicted by the theory of Prins but heretofore considered to be completely beyond experimental investigation. In another form (the four crystal spectrometer) a distinct improvement in spectral resolving power is anticipated. The new method of graphical analysis invented for the purpose of discussing these more complicated cases of polycrystalline x-ray reflection is conspicuously useful and clear as a help to understanding the two crystal spectrometer also. An experimental test of these new methods is now in progress.

Introduction

It is generally believed that the high resolving power of the two crystal x-ray spectrometer permits of no substantial improvement by any extension of its principle of operation. The author here proposes to show by a simple analysis of the action of repeated successive x-ray crystal reflections occurring at or near the Bragg selective angle that this is not the case.

Let us distinguish two classes of x-ray problems and correspondingly two kinds of resolving power which latter we shall call *angular resolving power* on the one hand and *spectral resolving power* on the other hand. In the first class come studies of the diffraction patterns of crystals. Darwin,[1] Ewald,[2] Prins[3] and von Laue[4] have contributed to the theory of such diffraction patterns while on the experimental side the widths of "rocking" curves in the "parallel position" have been studied by Ehrenberg and Mark,[5] Bergen Davis and H. Purks,[6] Allison and Williams,[7] and many others.[8] Von Laue has shown[9] that the two crystal spectrometer in the parallel position is incapable of revealing any asymmetry in the single crystal diffraction pattern if such asymmetry exists as the theory of Prins predicts. One of the purposes of the present paper is to show that by an extension to the use of three successive crystal reflections the asymmetric diffraction patterns of Prins can be experimentally studied. In the second class of problems come refined studies of spectral line shapes and spectral distributions in general such for example as the shape of the foot of the continuous x-ray spectrum. Here spectral resolving power is the essential consideration. In the first class of problems we aim to study how the reflecting power of a crystal for an ideal monochromatic parallel beam varies with slight deviations of grazing angle near the Bragg angle. In the second class of problems we aim to study how the intensity associated with a given wave-length in a beam of x-rays varies with the wave-length.

With a single crystal spectrometer the finite natural breadths of x-ray lines prevents the study of most crystal diffraction patterns almost entirely while the finite size of the crystal diffraction pattern would even with extremely fine slits place a serious limitation on the accurate study of spectral line shapes. To some extent the invention of the two crystal spectrometer removes these limitations and permits a partial separation of the dependence of reflected intensity on the two variables θ and λ. We propose to show here how a generalized extension of the two successive crystal reflections can be made to yield an even more complete separation.

Graphic Method of Analysis

The author has found that purely analytic expositions of the physical optics of the two crystal spectrometer are so involved and difficult that an extension of the problem to the case of more than two successive reflections has led him to invent the following simplified graphic method of thinking. Unquestionably the exact solution of any given configuration of crystal reflections can still best be obtained by writing down the integrals involved but before this point is reached the graphic method here described has great heuristic value as a help in the *choice* of configuration to be analyzed and as an aid to intuitive prediction of the interesting or uninteresting character of the result. The author believes also that the exposition of the physical optics in the simpler case of the two crystal spectrometer is greatly simplified by the use of this graphic method. The reader is urged to familiarize himself with its use as a tool in his thinking without which the present paper will be unintelligible.

Figure 1 represents a plot of the Bragg equation

$$n\lambda = 2d \sin \theta \tag{1}$$

the ordinates and abscissae being λ and θ, respectively. The individual curves correspond to the different orders n of reflection. Now the

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[1] C. G. Darwin, Phil. Mag. **27**, 325, 675 (1914).

[2] P. P. Ewald, Ann. d. Physik **54**, 519, 577 (1917); Zeits. f. Physik **2**, 232 (1920); **30**, 1 (1929); Physik. Zeits. **26**, 29 (1925).

[3] J. A. Prins, Zeits. f. Physik **63**, 477 (1930).

[4] M. von Laue, *Ergebnisse der Exakten Naturwiss.* (Julius Springer, Berlin, 1931), Bd. X, pp. 137–158.

[5] Ehrenberg and Mark, Zeits. f. Physik **42**, 807, 823 (1927).

[6] Bergen Davis and H. Purks, Proc. Natl. Acad. Sci. **13**, 419 (1927).

[7] Allison and Williams, Phys. Rev. **35**, 1476 (1930).

[8] S. K. Allison, Phys. Rev. **41**, 1 (1932); L. G. Barratt, Phys. Rev. **41**, 561 (1932); Mark and Von Susich, Zeits. f. Physik. **65**, 253 (1930); Kirkpatrick and Ross, Phys. Rev. **43**, 586 (1933). No attempt is made at an exhaustive list of this literature which is very extensive.

[9] Von Laue, Zeits. f. Physik. **72**, 472 (1931).

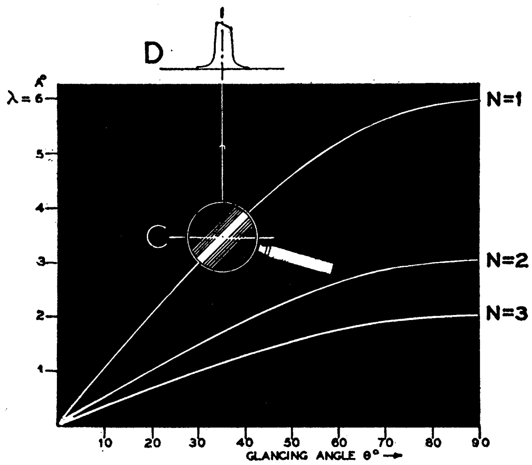

FIG. 1. Illustrating how the reflection properties of a crystal at various angles θ for various wave-lengths λ may be visualized as a function distributed over a plane cartesian coordinate system. The function will be nearly zero (black) save in regions close to the curved loci. As an aid to clarity we plot the regions of 100 percent reflection completely transparent and represent intermediate reflection coefficients with intermediate degrees of partial transparency. Such a graph we call a transparency graph. The striped effect seen in the magnifying glass is an effort to indicate the smooth gradation from almost complete transparency to opacity which cannot be otherwise indicated in a line drawing.

more refined *physical optics* of x-ray reflection teaches us that the connection between λ and θ is not quite rigid. For a given λ reflection at a crystal surface occurs over a small *range* of θ in the vicinity of the Bragg angle with varying degrees of intensity (diffraction pattern of the crystal) so that in a strict sense we must regard λ and θ as *independent variables*. The x-ray intensity reflected by the crystal is then to be thought of as a function of *both* λ and θ regarded as independent of each other. We must think now of a variable representing the intensity of reflection distributed all over the surface of the λ, θ plot of Fig. 1, but with values differing appreciably from zero only in the close vicinity of the lines on this plot. It will soon be apparent that the most helpful way to think of this intensity distribution over λ and θ is to represent it as a transparency. Regions of the plot where the reflecting power is unity are to be conceived as perfectly transparent while regions of zero reflecting power are opaque, with intermediate values grading between complete transparency and complete opacity. If then we examine a magnified cross section of one of the transparent traces along a line for which λ equals a constant as at C on our plot we would obtain the curve shown at D representing the transparency as a function of θ on this line. The shape of this curve is the diffraction pattern of the crystal for the wave-length and angle region indicated on the plot. We shall here make the assumption that a plot such as we have just described gives a *complete* description of the properties of a single crystal x-ray reflection.

This latter assumption is admittedly not rigorous. The author is well aware that more than two independent variables λ and θ are rigorously required to represent completely the intensity of reflection of a given crystal for a plane monochromatic beam of wave-length λ incident at angle θ_1 because the reflected beam may, in general, with reduced intensity, have a direction other than that required by geometrical optics so that a grazing angle θ_2 not necessarily equal to θ_1 and an azimuth ϕ measuring the departure of the plane of the angle of reflection from the plane of the angle of incidence are required. Thus strictly the intensity of reflection is a function of four independent variables, λ, θ_1, θ_2, and ϕ. In this paper however we are making the assumption that the one-to-one correspondences represented by the relations $\theta_1=\theta_2$ and $\phi=0$ are fulfilled so much more rigorously than is the one-to-one correspondence between λ and θ_1 represented by the Bragg Eq. (1) that the description in terms of λ and θ_1 alone is sufficient for our present purpose. All the conclusions of the present paper stand or fall according as this assumption is justified or unjustified. Of the two assumptions that of the one-to-one correspondence between θ_1 and θ_2 is by far the most important. There are good experimental reasons for hoping that this assumption is justified for good crystals of "perfect" type, chief among which is the extreme angular narrowness of the two crystal spectrometer rocking curves of good calcite in good accord with the theoretical predictions and their nearly triangular shape in cases where the single crystal diffraction pattern required by theory approximates a rectangle.

CASE OF TWO SUCCESSIVE REFLECTIONS, ANTIPARALLEL POSITION

With this understanding then a transparency plot such as Fig. 1 gives a complete description of the intensity of a single crystal reflection for all possible values of λ and θ. Consider now for the same beam of x-rays two such reflections occurring successively at two crystal reflecting surfaces. There will exist two similar plots like Fig. 1 for these two reflections. (We shall discuss here only the case where all crystals have identical transparency graphs though this graphical method handles the case of crystals having *different* graphs with equal ease.) Referring to Fig. 2 the two successive crystal reflections are denoted by A and B. It is evident that with the crystals stationary in the antiparallel position here shown an *increase* of the angle θ_A corresponds to a *decrease* in the angle θ_B *of equal magnitude*. If the dihedral angle is ω between the faces of the two crystals then when $\theta_A=0$; $\theta_B=\omega$ and when $\theta_B=0$; $\theta_A=\omega$. Also the final intensity after two reflections is the product of the intensity of reflection at each one. With the two crystals at a fixed angle ω the bicrystalline reflection still involves only two variables λ and either θ_A or $\theta_B=\omega-\theta_A$. The entire situation can thus be represented by superposing the two transparency graphs with their θ coordinates mutually reversed and displaced so that where $\theta_A=0$; $\theta_B=\omega$ and where $\theta_B=0$, $\theta_A=\omega$. It is evident that with such a reversed superposition the two graphs together will be everywhere opaque save in the small quasi-quadrilateral regions where the transparent traces on the individual graphs mutually intersect. An attempt to illustrate this situation in these pages would result in a black rectangle with a few small, symmetrically disposed, isolated, white patches dotted about on its surface, so the reader is requested to accept, instead, the graph of Fig. 3 in which the entire set of traces on each of the two reversed superposed graphs appears as black lines. The reader should however mentally substitute for this figure the picture of the two reversed superposed transparency plots in which light can only be transmitted through the intersections of the transparent traces. It may be even helpful for the reader to construct two or more such plots and actually superpose them. It will then be apparent how the transparent intersections move up and down along the wave-length scale when the upper plot slides horizontally over the lower plot corresponding to variation of ω the dihedral angle between the crystals. This illustrates the action of the two crystal spectrometer when exploring a spectrum in the antiparallel position. A spectral line can be thought of as a uniform horizontal line source of light directly behind the two superposed graphs at a height on their vertical wave-length scale corresponding to the wave-length of the spectral line to be represented. Sliding one graph over the other then causes the small transparent intersection or window to travel vertically over the spectral line and by plotting the total transmitted intensity as a function of the displacement of the transparency graphs the "shape" of the

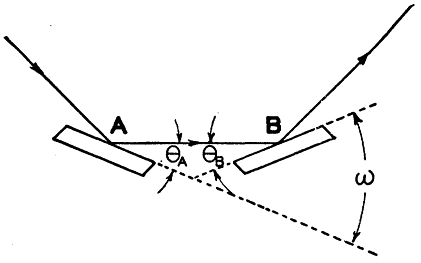

FIG. 2. Geometrical relationships in the two crystal spectrometer, antiparallel position.

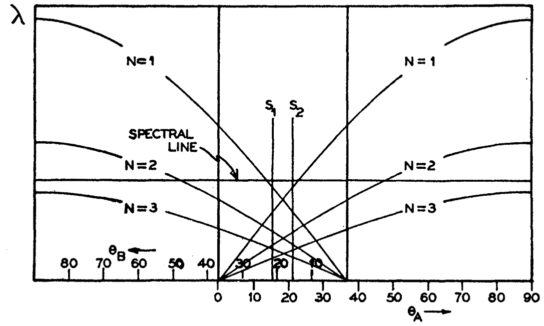

FIG. 3. Action of the two crystal spectrometer in the antiparallel position analyzed by the method of transparency graphs. The two systems of traces here shown in black lines must be imagined as if on two separate sheets of paper with the lines transparent and the background opaque so that light can only penetrate at the intersections of the transparent traces. A spectral line is represented as a horizontal line source of light immediately behind the charts at a height corresponding to its wave-length. Rocking the crystals corresponds to sliding one sheet over the other horizontally so that the "window" formed by an intersection moves vertically and explores the shape of the spectral line.

line is explored (the more faithfully the more restricted the window). What we may call rather freely the *area* of each window formed by the intersection of two graphs of order (n, m) is a measure of the total x-ray intensity which can be transmitted through the bicrystalline reflection in the (n, m) order. This "area" is in fact a surface integral of the product of the two intensity functions on the two superposed graphs since the quasi-quadrilateral transparent region in general has no sharp boundaries but fades off gradually on the sides into complete opacity. That such an integral really measures the total intensity transmitted through the bicrystalline reflection can be seen from the fact that on the graph it consists of weighted elements of extension $d\lambda$ in the vertical direction and of extension $d\theta$ in the horizontal direction and these on the two crystal spectrometer are precisely the elements that determine the total intensity since the solid angle under which the source can send radiation into the ion chamber is proportional to $d\theta$ and the spectral range which can be used in the source is proportional to $d\lambda$.

It is usual in the two crystal spectrometer to introduce lead stops so disposed as to place rough limitations on the horizontal angles of incidence and reflection at the two crystal surfaces. The effect of these can roughly be introduced into our superposed graph concept by including in the discussion only that part of the graph between the two vertical lines, such as S_1 and S_2 Fig. 3 which limit θ_A and θ_B in a way roughly similar to the lead stops. Two or more intersection points in the same vertical line however are thus active *simultaneously* in spite of this stop limitation. This superposition of the (2, 2) order spectrum upon the (1, 1) order is a pitfall which is well known and can be avoided usually by appropriate choice either of filters or of the voltage used to excite the x-rays so as to suppress the unwanted order.

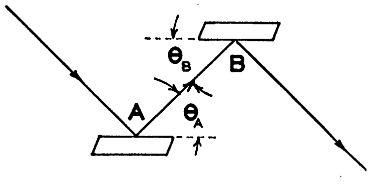

FIG. 4. Geometrical relationships in the two crystal spectrometer, parallel position.

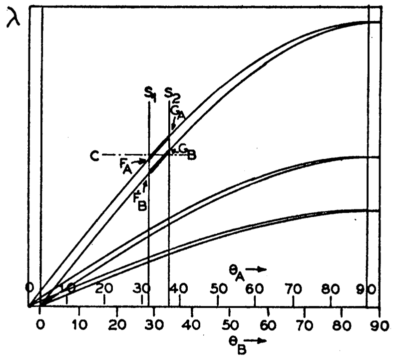

FIG. 5. Action of the two crystal spectrometer in the parallel position analyzed by the method of transparency graphs. The graphs are here shown mutually displaced from the position corresponding to complete parallelism so that they can be distinguished separately in a drawing.

Throughout the present paper the vertical divergence of the x-ray beam is supposed to be held constant and sufficiently small so that it need not be discussed.

CASE OF TWO SUCCESSIVE REFLECTIONS IN THE PARALLEL POSITION

In Fig. 4 two crystals are shown in the "parallel" position. It is evident here that with the crystals fixed at or near parallelism an increase of θ_A produces a corresponding equal increase in θ_B. It is therefore evident that we must superpose our transparency graphs with their θ scales increasing in the same sense (say from left to right). In Fig. 5 again we substitute a black line graph of the situation and request the reader either in imagination or in reality to construct the corresponding directly superposed transparency graphs. The use of lead stops and shields will again place a rough limitation on the angle θ indicated by the two vertical lines S_1 and S_2 so that only the narrow region on the plot between these limits will be under discussion. By the appropriate choice of voltage on the tube and the use of a target with strong emission lines whose wave-lengths are selectively reflected in the desired order (say the first) at angles included in the region between S_1 and S_2 the entire x-ray intensity can be restricted to one small region of say the first order branch of the transparent loci, such as the regions F_A, G_A and F_B, G_B in Fig. 5. Now if we slide the two transparency graphs horizontally until the arcs F_A, G_A and

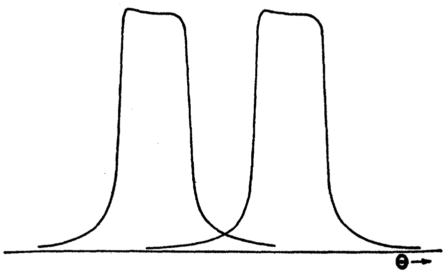

Fig. 6. Enlarged profile of the intensity of reflection taken along the horizontal line C in Fig. 5. where it cuts the two arcs F_AG_A and F_BG_B.

F_B, G_B coincide identically a maximum intensity can pass through the elongated window formed by the complete superposition of these transparent traces. All spectral lines and all of the continuous spectrum falling in the region traversed by the arc F, G can shine through the window whose "area" is seen to be far greater than the small quadrilateral areas of windows formed by intersections in the antiparallel position (Fig. 3).

Let us take a horizontal section as at C Fig. 5, and plot the transparency across each of the traces at this section. Fig. 6 shows these two cross sections or diffraction maxima from the two traces, the shape illustrated being the prediction of the theory of Prins for Mo K-radiation reflected in the first order on the cleavage planes of calcite.[10] Over the small range F, G, a horizontal cross section through the traces taken at any point whatever will have substantially the same shape as that shown in Fig. 6 since the shape of the diffraction pattern does not in general vary rapidly with wavelength. Therefore when the transparent graphs of Fig. 5 are displaced horizontally so that these graphs pass through complete coincidence (exact parallelism of the crystal reflecting planes) the behavior of the intensity transmitted through the graph as a function of the displacement can be readily inferred by displacing the profiles of Fig. 6 across each other and plotting the product integral over the two overlapping curves as a function of their displacement as indicated in the successive positions A, B, C, D and E, Fig. 7. The curve so obtained is the familiar rocking curve in the parallel position of the two crystal spectrometer and it is immediately apparent why, even with asymmetric single crystal diffraction profiles, the rocking curves are necessarily symmetrical since the paired configurations on either side of the coincidence point C are identical.

The Principle of Sharpening by Slightly Displaced Superposition of Diffraction Patterns

Suppose now that the transparency graphs of Fig. 5 are only *slightly* displaced away from the position of exact coincidence so that a horizontal cross section of the two transparency graphs looks like the case B or D of Fig. 7. The super-

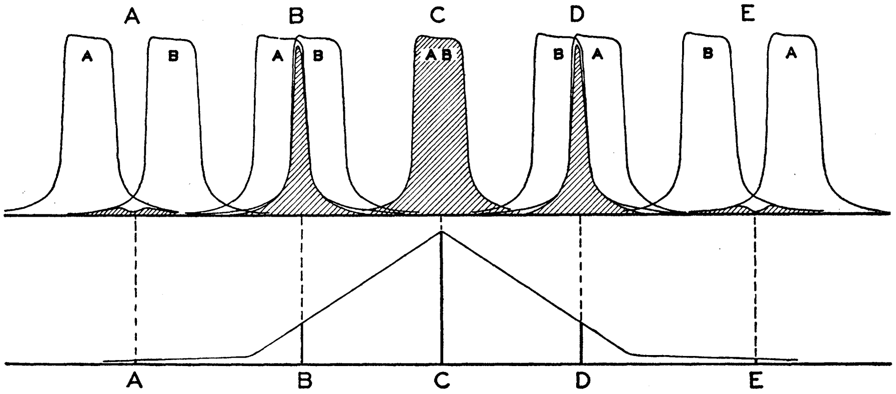

Fig. 7. Illustrating the variation of reflected intensity with various degrees of overlapping of the diffraction patterns of crystals A and B as the crystals are rocked through the parallel position. The values of the product integrals plotted as ordinates in the lower curve correspond to the total superposed transparency "area" available with different degrees of overlapping of the transparent traces F_AG_A and F_BG_B as the graphs of Fig. 5 slide over each other.

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[10] The profile here shown is taken from Compton and Allison's book *X-Rays in Theory and Experiment*, page 386.

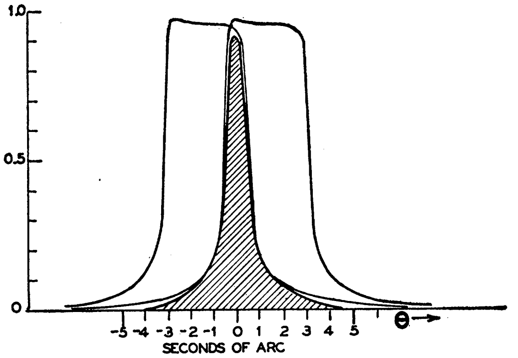

FIG. 8. The principle of "sharpening" by appropriate displaced superposition of diffraction patterns. The shaded profile is the product of multiplying the ordinates point by point on the two unshaded curves.

position of these two transparent traces in this fixed position will yield a composite trace whose horizontal profile we obtain by constructing the point by point *product* of the ordinates of the two slightly displaced curves to yield the heavy shaded profile shown in Fig. 8. If the displacement is judiciously chosen it is evident that this resultant product *will be a very much narrower curve* than either of the factors while retaining almost the original maximum height because the maximum heights of the Prins traces correspond nearly to unity. Thus under these conditions the beam of x-rays after two reflections, though it is neither monochromatic nor unidirectional *possesses a much sharper relationship between direction and wave-length* than did the beam after only one crystal reflection. *It may thus be regarded as a sharpened tool with which to explore the diffraction pattern of a third crystal.* This leads to the application of our transparency charts to the theory of the three crystal spectrometer for the study of the asymmetric diffraction patterns of Prins which up to the present have been thought to be undetectable.

Bollman and Bailey have found experimentally with three calcite crystals reflecting Mo K-radiation on their cleavage planes and have subsequently verified by graphical integration with the theoretical diffraction patterns of Prins that the simple application of the principle of displaced superposition of diffraction patterns is not enough to give a "tool" adequate satisfactorily to reveal the Prins diffraction pattern of a third crystal. When the core of the composite diffraction pattern of the two crystals constituting the tool has been narrowed down by displaced superposition the importance of the side fillets or wings is relatively so much increased as to necessitate a special procedure to remove their distorting effect. The details will be given in a paper describing the experimental results.

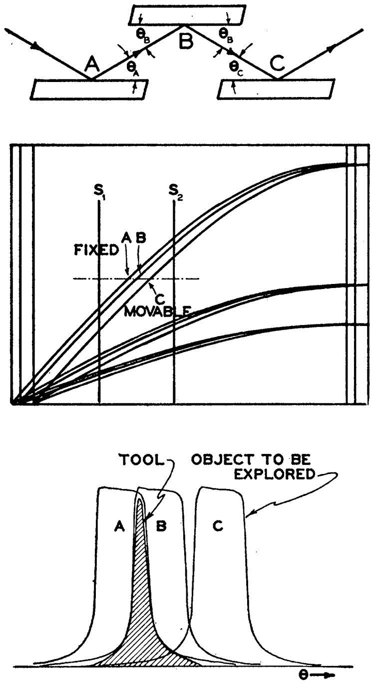

FIG. 9. Geometry of the three crystal spectrometer (parallel case), its triple transparency graph and the profiles of tool and object to be explored.

THE THREE CRYSTAL SPECTROMETER

Figure 9 shows the disposition of x-ray beams and crystals A, B, C to form the three crystal spectrometer. With these crystals in fixed relation to each other and with their reflecting planes very nearly in mutual parallelism it is evident that increasing the angle θ_A *increases* the angles θ_B and θ_C by exactly the same amount. Hence the transparency graphs for the three reflections must be superposed with their scales of θ all increasing in the same sense (say from left to right). If we displace crystal B say three seconds of arc away from strict parallelism with crystal A then transparency graphs A and B will be displaced from exact coincidence in such a way that the transparent trace formed by the superposition of the two graphs will be much narrower than before. Crystals A and B are thenceforth held in fixed relation to each other and the beam which has been successively reflected from both of them now has the sharpened relationship between wave-length and direction represented by the narrower trace on the transparency graph. With this beam falling on the reflecting face of crystal C the latter is now rocked through a small angular range and the intensity after three reflections is plotted as a function of this rocking angle, a sufficient range being covered to completely explore the resultant pattern. This is equivalent to sliding the graph C over the fixed displaced pair of graphs A and B and because of the narrowness of the composite trace formed by A and B it becomes a sufficiently sharp tool to reveal with considerable fidelity the features of the horizontal profile of the trace on graph C. In this process reflections A and B furnish what may be described as the exploring tool while reflection C is the object studied. But it is immediately evident from the concept of the transparency graphs that *any* pair out of the three crystals may serve as the tool by giving this pair the appropriate displacement from parallelism and fixing its members in this displaced position while the third crystal is rocked and the intensity of the tricrystalline reflection is plotted as a function of this rocking angle. The pair of reflections constituting the "tool" need not be an adjacent pair since the total intensity depends simply on the product of the intensities of reflection on the three graphs and therefore obeys the commutative law of multiplication. Thus the three crystal spectrometer affords a ready method of studying the diffraction patterns *of all three* crystals separately with equal ease. True, the results are only *first approximations* to the true diffraction pattern since the sharpened tool in each case cannot be infinitely sharp and in practice will probably never be less than say one-tenth the width of the diffraction patterns themselves. However there is this immense advantage in getting these first approximations to the diffraction pattern shapes of all three crystals, namely that the approximate profiles of any pair used as a tool can now be applied to determine (by multiplying them together) the approximate shape of that tool. The approximate profile of the third crystal can then be *corrected* (by the solution of an integral equation) since the shape of the tool with which it was explored is known. This method would give a second approximation to the profile of each crystal and this can of course be obtained for all three profiles. It is easy to see therefore how by an iteration method it would be at least conceptually possible to get, through repeated approximations, an accurate, completely resolved profile for all three crystals. We are not yet in a position to say how practical such a scheme might turn out to be. The solution of integral equations with data of limited accuracy is frequently disappointing, but the conceptual possibility of an iteration process in the three crystal case is worth mentioning since it is quite impossible in the two crystal case.

It need scarcely be added that the rocking profile, obtained by rocking any one of the three crystals such as C with the other two crystals A and B in fixed slightly displaced nearly parallel relationship, should be studied for several degrees of displacement of the tool pair AB. If any asymmetry in the rocking profile appears then that displacement of AB which yields most

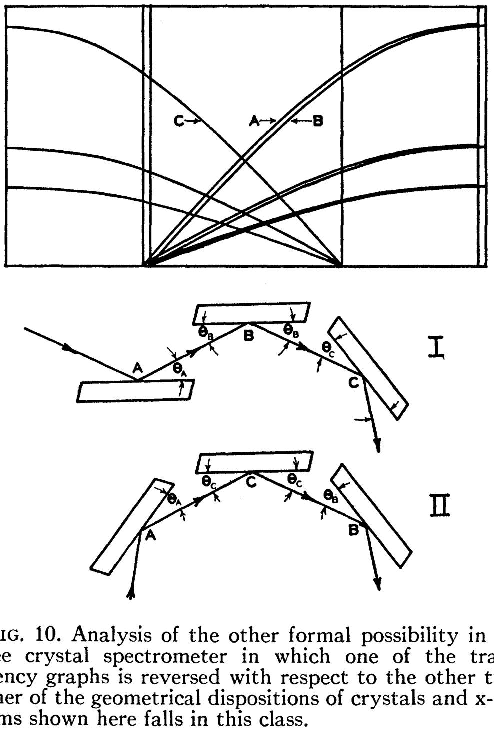

FIG. 10. Analysis of the other formal possibility in the three crystal spectrometer in which one of the transparency graphs is reversed with respect to the other two. Either of the geometrical dispositions of crystals and x-ray beams shown here falls in this class.

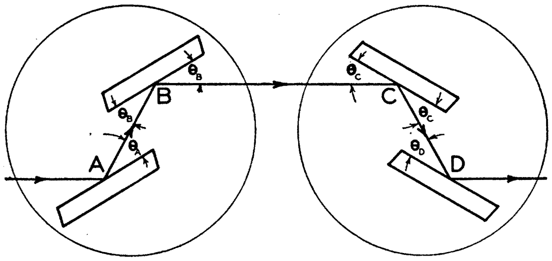

FIG. 11. The most interesting of several possible dispositions of crystals and reflections in the four crystal spectrometer.

pronounced asymmetry seems likely to be the most favorable one for use as a tool.

So much for the three crystal spectrometer with all three reflecting surfaces mutually parallel so as to call for transparency graphs with angle scales all increasing in the same sense. Much less interest attaches to any other possible three crystal configuration. Indeed the properties of the only other arrangement of three crystals which can be regarded as truly distinct from the foregoing one are obviously obtained by reversing the sense of the angle scale of one of the transparency graphs. This leads to a situation like the one shown in Fig. 10 for which the author can see no especially interesting application at present.[11]

Thus the three crystal spectrometer gives an improvement over the two crystal spectrometer in angular resolving power offering the possibility of studying the asymmetric diffraction patterns predicted by Prins but no great improvement in *spectral* resolving power can be expected from it. New and interesting possibilities however enter when we pass to the case of *four* successive crystal reflections.

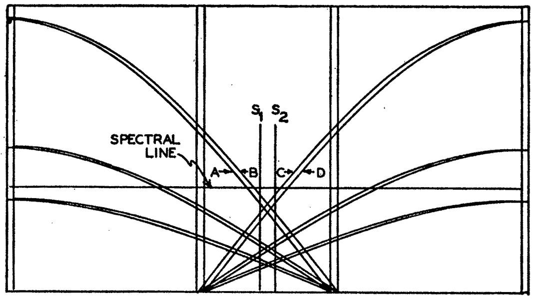

FIG. 12. Transparency graph for the four crystal case of Fig. 11.

THE FOUR CRYSTAL SPECTROMETER

Figure 11 shows the most interesting of several possible dispositions of crystals and reflections with four crystals A, B, C, and D. With all four crystals in fixed relationship it is apparent that increasing θ_A increases θ_B but decreases θ_C and θ_D. Hence the transparency graphs are to be superposed with one pair A, B having the angle scales of its members increasing in one sense while the remaining pair C, D has the angle scales of its members increasing in the opposite sense. Each pair, by the method of slightly displaced superposition already described, now can be made to constitute a sharpened tool. The members of each pair are therefore to be held in rigid mutual geometrical relationship but the pairs are rocked as a whole, the one with respect to the other, so that a spectrum can be explored. The result is easily understood in terms of the transparency graphs. The black lines of Fig. 12 are as before substituted for the transparent traces, the pairs of traces whose

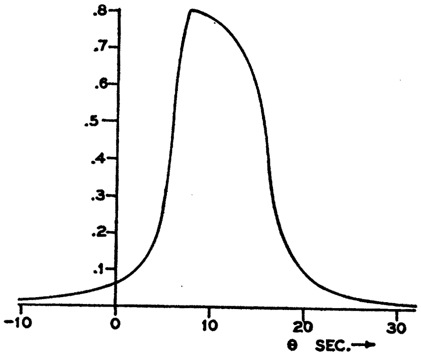

FIG. 13. Profile of the diffraction pattern of 2.3A x-rays, unpolarized, reflected from a calcite cleavage face as predicted by Prins theory. Taken from Compton and Allison *X-Rays in Theory and Experiment.*

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[11] The equivalent configurations of crystals and beams I or II in Fig. 10 *do* offer the possibility of increasing the *wave-length resolving power* to a small extent over the best attainable in the two crystal spectrometer. Consider the case where all three crystals are used in the same order. Referring to the transparency graph of Fig. 10 it is easy to see that the vertical extension of the window formed by the intersection of the two partially overlapping traces A and B with the third trace C *can never be made less than half the vertical extension for two intersecting traces* no matter how thin the composite trace AB is made by the judicious choice of the displacement of its components. This limitation is however removed in the four crystal arrangement which we are about to discuss. It is possible that for special cases even this slightly increased wave-length resolving power which the three crystal arrangements of Fig. 10 afford coupled with the greater economy of x-ray intensity available with three reflections as compared to four may make this configuration of some utility.

members lie closely adjacent representing respectively the parallel pairs *A*, *B*, and *C*, *D*. The reader will understand of course that although the members of a pair of adjacent traces are shown in Fig. 12 as distinctly separated he is to think of them as superposed in the manner already described with only a very slight displacement of such amount that the total effect of this displaced pair is to give a much narrower transparent trace than either member alone would give.

The four crystal spectrometer is then in effect a two crystal spectrometer with pairs substituted for each of the two single crystals so that the result is the same as though two crystals with very much narrower diffraction patterns had been used. On the transparency graphs the narrow traces formed by the displaced pairs cross to form windows of much smaller dimension in the vertical (or wave-length) direction with a consequent increase of spectral resolving power.

The reduction in the size of the quadrilateral shaped window at the fourfold intersection on the transparency graph means a serious reduction in available x-ray intensity. It is unfortunate, but apparently unavoidable, that an *n* fold increase in resolving power by this method results in diminishing the available intensity through multiplication by a factor n^{-2}. An increase in resolving power is thus paid for rather dearly.

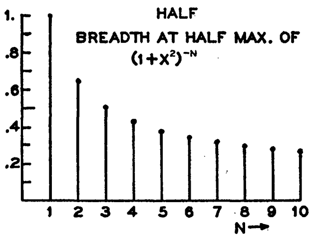

FIG. 14. Showing how raising the "witch" equation to higher and higher powers, *n*, progressively decreases the half-breadth at half-maximum height of the resultant curve.

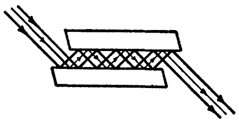

FIG. 15. A simple method of applying experimentally the principle of undisplaced superposition for sharpening the traces on the transparency graph.

THE PRINCIPLE OF "SHARPENING" BY REPEATED UNDISPLACED SUPERPOSITION OF DIFFRACTION PATTERNS

So far we have described only one method of sharpening or narrowing the traces on the transparency graph, that of displaced superposition of two traces. Now this method is most appropriate the nearer the horizontal profile section of a single trace approximates *a rectangular shape*. For traces like those in Fig. 6 which depart insignificantly from being rectangular by some asymmetry at the top and a little transition "fillet" on either side it is evident that a strong sharpening effect can be obtained by displaced superposition. On the other hand if the trace profile more nearly resembles the curve commonly known as the "witch," $y=(1+x^2/a^2)^{-1}$ the author has verified mathematically that no help can be expected from the use of displaced superposition of such profiles. In point of fact the Prins theory predicts that the trace profiles do indeed become more and more witch-like for longer wave-lengths, Fig. 13 being an example for the case of 2.3A units reflected from a cleavage face of calcite. When two equal witches with half-breadths, *a* (at half-maximum height), are superposed with increasing mutual displacement 2δ it turns out that when $\delta=a$ the product or resultant of the two curves just begins to manifest a double peak and is therefore thenceforth an undesirable exploring "tool" for most purposes. Restricting ourselves therefore to displacements $|\delta|<|a|$ it is easy to show that the resultant curve is always broader at half of its maximum height than is either one of the component curves at half of its maximum height. We must then in the case of such profiles fall back on another and perhaps somewhat less promising method of sharpening the trace. This consists in superposing, *in exact coincidence*, a number of similar witch-like profiles. The resultant curve will be narrowed simply because the wings of the curve have numerical values considerably less than unity for the intensity of reflection so that the product of multiplying many such factors will be relatively more strongly suppressed than will be regions of the

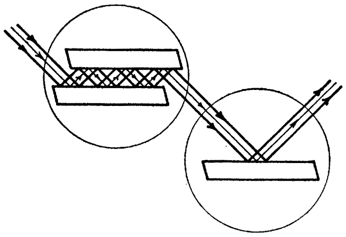

FIG. 16. Method of applying the principle of sharpening by undisplaced superposition to increase the angular resolving power in the three crystal spectrometer.

curve near the maximum where the values are more nearly unity. Fig. 14 is a graph showing how the half-breadth, a_n of a witch at half-maximum height diminishes as we raise the analytical expression for the curve to higher and higher powers, n. The process is one which yields rapidly diminishing returns in x-ray intensity because even the maximum of such witch-like profiles is not unity and the area under the profile therefore diminishes more rapidly than the breadth. Fig. 15 shows a simple way of realizing such a sharpening by repeated undisplaced superposition of the transparency traces. The crystals A and B must be of high quality absolutely free from mechanical strain so that the crystal planes will approach being mutually parallel over their entire reflecting surfaces to the highest degree. One plans beforehand how many successive reflections are desirable and knowing the Bragg angle to be investigated the appropriate separation between the reflecting faces can be computed to give this number of reflections. The transparency graphs for all these reflections evidently have their θ scales in the same sense. The state of parallelism of the two crystals can be determined of course directly by plotting the intensity of the x-ray beam after the n parallel reflections as a function of the rocking position of one of them with respect to the other. It is scarcely necessary to point out that this principle of sharpening can be applied to the three crystal combination for the study of diffraction patterns or to the four crystal arrangement for improving spectral resolution. Figs. 16 and 17 show the disposition of crystals and x-ray beams appropriate to these two applications.

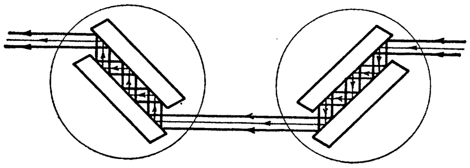

FIG. 17. Method of applying the principle of sharpening by undisplaced superposition to increase the spectral resolving power in the four crystal spectrometer.

NOMENCLATURE

It is regrettable that the choice of notations of Allison and Williams for the two crystal spectrometer does not stand the test of generalization to more than two successive reflections. If these authors had chosen the convention of algebraic signs so that, for example, working in the first order on both crystals in the antiparallel position was denoted $\{1, -1\}$ instead of $(1, 1)$ (with $\{1, 1\}$ for the parallel position) then this notation could have been generalized very satisfactorily. It is clear that the prime requisites of a notation are: 1. that equivalent situations shall be denoted by equivalent symbols, and 2. that different situations shall be denoted by different symbols. Allison and Williams' notation only meets the second requirement. *It should be amply evident by now that the essential character of a given configuration of crystals and beams, both as to its properties for resolving wave-lengths and its angular resolution, turns uniquely on the type of trace intersection (or coincidence) required to represent that configuration on the transparency graph.* Hence a complete specification of the situation is given by stating the order number of each trace and assigning an algebraic sign to each order number representing whether the θ scale on the transparency graph for that particular trace increases from left to right or from right to left. Reversal of all signs in a given symbol in this notation leaves the situation unchanged so that the arbitrary convention of always writing the first-order number in the symbol positive can be retained. In this new convention the *sequence* in which the order numbers are written is immaterial for the complete description of the transparency graph. Thus the configurations I and II of Fig. 10 which for both angular and spectral resolution are entirely equivalent would in the new notation be denoted $\{1, 1, -1\}$ and $\{1, -1, 1\}$, respectively. Their equivalence is thus immediately apparent in their symbols. To avoid confusion with the notation of Allison and Williams the author suggests the use of braces for the new notation.[12]

OTHER POSSIBILITIES

Some four years ago Paul Kirkpatrick suggested to the author the possibility of obtaining increased x-ray resolving power by the use of a number of similar crystals standing on an arc of a circle arranged in a succession like that indicated in Fig. 18, the crystals being so orientated that all the dihedral angles between any two adjacent crystals are equal. It was his idea to provide a mechanism so that this dihedral angle common to all adjacent pairs could be varied for all the crystals at once, their centers of rotation being simultaneously shifted so that the reflected beam would never leave the face of any crystal. In Fig. 18 two positions assumed by the arrangement as the angle is varied are shown.

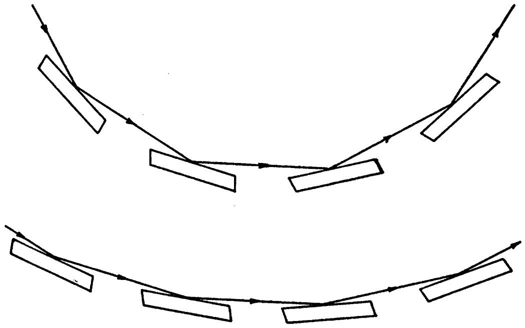

FIG. 18. Paul Kirkpatrick's suggested extension of the two crystal spectrometer.

ACKNOWLEDGMENTS

At the time Kirkpatrick made this suggestion the author had not yet invented the convenient method of thinking about such problems with transparency graphs described in this paper. An analysis of Kirkpatrick's suggested arrangement by means of transparency graphs shows that for the case of three crystals it is identical to the case analyzed in our Fig. 10 and hence is without great interest. For the case of four crystals Kirkpatrick's arrangement is identical in its results to our four crystal arrangement pictured in Fig. 11 and analyzed in Fig. 12. It seems to the author to have the disadvantage of being mechanically somewhat more difficult to realize than the solutions here proposed but the author feels deeply indebted to Professor P. Kirkpatrick nevertheless because this suggestion of his involving the use of more than two successive crystal reflections started the entire train of thought which has led the author to the analysis and conclusions of the present paper.

At the present writing work is well advanced by V. L. Bollman and the author in preparation for an experimental test of the three crystal arrangement of Fig. 9 studying the diffraction pattern of calcite.

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[12] To avoid all confusion we state below the rules for determining algebraic signs in Allison's notation and in our new proposed notation and a rule for transforming either notation into the other.

In Allison's notation the order number of the first reflection is always given the positive sign. As we proceed along the beam in the direction of propagation each succeeding reflection is called positive or negative according as the reflecting crystal is on the same side or the opposite side of the beam as is the first reflecting crystal.

In the new proposed notation the order number of the first reflection is always positive. As we proceed along the beam in the direction of propagation each succeeding reflection takes a sign opposite to its immediate predecessor if the crystal is on the *same* side of the beam as was the crystal in the immediately preceding reflection; or if the crystal is on the opposite side of the beam to its immediate predecessor its reflection takes the *same* sign as the immediately preceding reflection.

To transform either notation into the other reverse the signs of the second, fourth, sixth, etc. reflections and leave unchanged the signs of the first, third, fifth, etc. reflections.