"Thickness Effect" in Absorption Spectra near Absorption Edges*

L. G. Parratt, C. F. Hempstead,† and E. L. Jossem‡

Cornell University, Ithaca, New York

(Received September 28, 1956)

The details of an observed absorption spectrum are shown to depend upon the thickness of the absorber. This effect is present, at least in principle, regardless of the type of radiation involved. It is discussed here specifically for x-rays, and specifically for the neighborhood of an absorption edge. Measurements of widths and of relative intensities of the component structure are the most sensitively involved, but wavelengths are also slightly affected. The explanation lies in the rôle of the effective spectral window of the spectrometer. The effect may be serious when the "tails" of the window are extensive, as is inevitably the case with two-crystal x-ray spectrometers. Features of the extent and shape of the spectral window for the (1, +1) position of the instrument used in this work are roughly determined from the thickness effect.

INTRODUCTION

THE absorption spectrum for x-rays in the frequency region of an absorption discontinuity is rich in structural details of increasing interest in solid-state studies. To date, measurements have been confined almost exclusively to wavelengths of some arbitrary feature called the absorption edge, and of the several maxima and minima exhibited on the high-frequency side of the edge. As we try to bring into better focus the details of the relative intensities and spectral shapes, we encounter numerous instrumentation problems. In the present paper we point out a new effect: The details of the observed absorption spectrum depend upon the thickness of the absorber. This effect, as we shall see, is just another twist in the old problem of the instrumental resolving power.

CHOICE OF THICKNESS

In absorption structure work, the investigator seeks a curve of either the transmission I/I_0 or the absorption coefficient μ plotted against the photon frequency ν, where μ is obtained from the relation

$$I/I_0 = e^{-\mu x}, \qquad (1)$$

where x is the thickness of the absorber. Sometimes, when x is not known as accurately as is the product μx, he is content to use merely the product. But in either case, he must choose the thickness x in the design of his experiment.

To date it has been the wont of the x-ray spectroscopist to choose, when he can, an absorber thickness that allows the greatest precision in the product μx as calculated from the measured intensity ratio I/I_0. Several criteria for such an "optimum" thickness have been used, each of value as far as it goes. We shall mention briefly the three criteria that have been the

most popular; then we shall add a new criterion, one which deals with *accuracy* rather than with *precision* alone.

First, the measurement of the intensity ratio of two x-ray beams (having the same spectral composition) is essentially a photon-counting problem; and the well-developed statistics of counting apply. By this statistical theory, if the time involved in the measurement is assumed to be fixed, the absorber thickness that allows the greatest precision in μx is determined entirely by the ratio of the background counting rate to the incident-beam counting rate. This "optimum" thickness, x_c, is such[1] that the ratio of I/I_0 is about 0.07 if the relative background is negligible; this ratio increases nonlinearly as the background increases, and is about 0.2 if the relative background is about 0.1. The "optimum" thickness by this criterion is tied up in the product μx_c, Eq. (1), but can readily be determined if μ is known. Thus, for the case of negligible background,

$$x_c = -\ln(0.07)/\mu. \qquad (2)$$

In the study of a spectral region involving many different values of μ, we need, according to these statistical considerations, many absorbers each of a different "optimum" thickness. This leads to the second criterion.

For two different absorption coefficients, μ_1 and μ_2, for which the transmitted intensities are I_1 and I_2, we may write Eq. (1) with each of the two subscripts and solve simultaneously for the thickness x_d that gives the greatest intensity-contrast, i.e., that makes the difference $I_1 - I_2$ a maximum.[2] Thus, for $d(I_1 - I_2)/dx = 0$,

$$x_d = \frac{\ln(\mu_1/\mu_2)}{\mu_1 - \mu_2}. \qquad (3)$$

The "optimum" thickness x_d is based on an implicit assumption that measurements of I_1, I_2, and I_0 are all

[1] M. E. Rose and M. M. Shapiro, Phys. Rev. **74**, 1853 (1948).

[2] Alternatively, we could define contrast as the difference $\mu_1 - \mu_2$. Maximum contrast in this definition leads to a different "optimum" thickness x_c' which is given by the transcendental equation $e^z(z - y - 1) - e^y = \sqrt{2}$, where $2z = \mu_2 x_c'$ and $2y = \mu_1 x_c'$.

made with the same percentage precision, a condition that can be easily met if the time involved in each intensity measurement is adjusted appropriately. Since this precision condition is not the same as that assumed in x_c, the two values x_d and x_c are different.

In order to formulate a physical interpretation of an observed curve of μ vs frequency, one may wish to know precisely the ratio of two values μ_1 and μ_2 at particular frequency positions. Thus, a third criterion for "optimum" absorber thickness is that which results in the greatest precision in the ratio $r \equiv \mu_2/\mu_1$. Analysis, such as that carried out in reference 1, concludes that the optimum thickness x_r depends on the value of r as shown with four numerical examples in Table I. In this table, α_2 and α_1 are, respectively, the fractions of the total time spent in counting the transmitted beams for μ_2 and μ_1. The background has been assumed to be negligible. Note that the minimum transmission lies between 0.09 and 0.12 for all the values of r shown. Both the first and third criteria lead to the rule-of-thumb that about 10% minimum transmission is "optimum" when the background is low.

The presence of a substrate (which may be necessary to support the absorber), or of another element in a compound, further complicates the statement of an optimum thickness criterion. In general, additional absorbing media call for thinner absorbers.

These three criteria are based solely on precision of measurements. We shall see that, when our interest includes the physical meaning of the quantity being measured so precisely, an important additional problem arises in the choice of an optimum thickness: Distinction must be made between precise measurements and accurate measurements.

OBSERVED STRUCTURE

We recently recorded with a two-crystal spectrometer (an instrument having very high physical resolving power,[3] viz., $\lambda/\Delta\lambda \doteq 11\ 000$), the absorption spectrum of crystalline KCl in the region of the chlorine K edge. The absorption coefficient varies irregularly between extremes of about 650 cm^{-1} to about 3320 cm^{-1}.[4] We

TABLE I. Parameters for calculating optimum thickness x_r.

r	$\mu_2 x_r$	α_2	α_1
1	2.421	0.413	0.413
2	2.286	0.353	0.396
4	2.164	0.243	0.433
8	2.087	0.141	0.456

---

[3] Resolving power is conventionally defined as the wavelength divided by the full width at half-maximum of the spectral window regardless of the shape of the window. (In two-crystal x-ray spectrometry the width of the spectral window is taken as the width of the (1, −1) curve.) As we shall see in this paper, this numerical value of resolving power is optimistically misleading if the window has extensive tails. See reference 16.

[4] These measured coefficients are for an absorber consisting of 35×10^3 A of KCl on a thin substrate of polystyrene. The substrate alone has about 90% transmission at the Cl K-edge wavelength, 4.4 A.
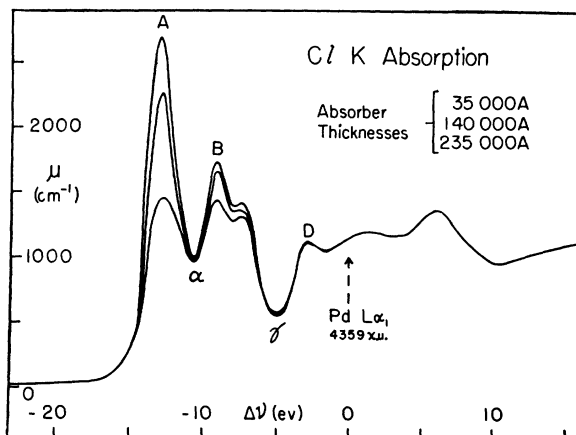

FIG. 1. Experimental absorption spectrum in the region of the K edge of chlorine in crystalline KCl. Three absorber thicknesses were used; in general, the thinner the absorber the greater the absorption coefficient. By the choice of the zero of the ordinate scale, the absorption coefficients refer to the chlorine K electrons only; the measured coefficients are obtained if 640, 410, or 370 is added to the numerical values for the 35×10^3 A, the 140×10^3 A or the 235×10^3 A curve, respectively. (The Pd $L\alpha_1$ line was used as a reference wavelength.)

were interested in the structural details in all parts of this spectrum, so, in choosing the absorber thicknesses, we were at first guided by the advice afforded by all of the criteria discussed above. For example, for the region of low absorption, x_c is 409×10^3 A from Eq. (2); for the region of high absorption, x_c is 80×10^3 A;[5,6] and for this range of extremes in μ, x_d is 61×10^3 A from Eq. (3).

Actually, as a start, we chose several values of x selected in the range from 235×10^3 A to 35×10^3 A. With each absorber thickness and for each value of I and of I_0 throughout the entire curve, sufficient counts were accumulated to make the probable error in μx less than one percent. The large value of I_0 (about 650 counts per second) made the time required to obtain this precision reasonably short even with the thinner absorbers. Nevertheless, we were prepared to believe that thicker absorbers would be better.

To check internal consistency in our observed curves, we ran the entire spectral region with each absorber thickness. Three of these curves are shown in Fig. 1. The shapes of the curves are in marked disagreement. After checking with new absorbers, different substrates, etc., we convinced ourselves that the effect is real. We call it the thickness effect.

---

[5] The transmitted counting-rate with our proportional-counter system was always rather large (e.g., a minimum rate of more than 200 counts per second with the 35×10^3 A absorber) so that the background rate, less than 0.2 count per second, was negligible. The x-ray tube, platinum target, was operated at 10 to 12 kv and 60 to 80 ma, with voltage and current separately stabilized electronically to better than 0.1% during each run.

[6] If $I_0(\nu)$ of Eq. (4), discussed later, is assumed to be essentially constant (i.e., a flat incident spectrum) and if this incident intensity is checked only occasionally during the run, x_c is a little less than the value calculated for $I/I_0 = 0.07$ in Eq. (2).
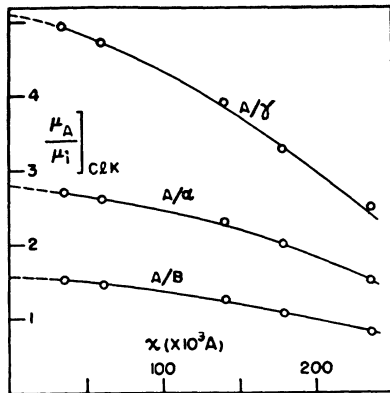
FIG. 2. Ratios of absorption coefficients (as featured in Fig. 1) depend upon the thickness x of the absorber. The coefficients refer to the chlorine K electrons only.

The disparity among the curves for different absorber thicknesses may be conveniently expressed in terms of the ratios of the maxima to minima, e.g., A/α and A/γ, and the maxima to maxima, e.g., A/B, using the Fig. 1 notation. Figure 2 shows how these three ratios vary with absorber thickness; in this figure the absorption coefficients are taken for the chlorine K electrons only (by subtracting off the appropriate μx "background").

It is apparent that we need a new criterion for "optimum" thickness. Since the thickness effect is negligible only for extremely thin (strictly, for zero thickness) absorbers, the new criterion says that the "optimum" thickness is the minimum value that can be satisfactorily prepared.[7] In practice, it behooves the investigator to keep in mind all these criteria for "optimum" thickness, and not to rely exclusively on any one of them. He must exercise delicate good judgment if he wishes high accuracy in his final curve.

EXPLANATION OF THE THICKNESS EFFECT

The explanation of the thickness effect lies in the solution of an old spectroscopic problem, i.e., in the role of the spectral window of the spectrometer.[8] By "spectral window" is meant the effective over-all spectral response of the instrument. If the beam incident

[7] In going to an extremely thin absorber, the investigator must beware of other effects such as the nonuniformity of thickness. Nonuniformity also distorts the absorption structure and results in inaccurate values of the absorption coefficients. In very thin absorbers, the microscopic nonuniformity may be of greater concern than the macroscopic. For example, our KCl absorbers were prepared by the vacuum evaporation technique and it is known that such a condensed KCl film consists of randomly oriented crystallites. If the average crystallite size is about 10 000 A, a film of nominal thickness 35 000 A probably contains a nonuniformity that is just on the verge of being intolerable.

[8] That the spectral window distorts the true spectrum has been known since the beginning of spectroscopy, and many attempts to analyze the effects have been made. Most of these attempts have assumed a simple window function, for example, a rectangle or a triangle, and have assumed a simple emission or absorption line, often Gaussian in shape. See S. Brodersen, J. Opt. Soc. Am. **44**, 22 (1954) and references therein. Also, R. C. Spencer, Phys. Rev. **48**, 473 (1935), discusses Lorentzian functions; and F. D. Kahn, Proc. Cambridge Phil. Soc. **51**, 519 (1955), treats some other symmetrical windows.

on the spectrometer has a flat spectrum, the spectral window may be interpreted as the function which gives the relative probability that a photon of energy $h\nu$ will be counted when the spectrometer is set at energy $h\nu_s$. So defined, the spectral window includes, along with the crystal diffraction pattern(s), the geometrical effects of the horizontal and vertical slits, diffuse thermal scattering by the crystal(s), spurious scattering from any source, and the relative sensitivity of the detector. The true transmission is distorted by the spectral window by an amount that depends, of course, upon the window's width and shape.

If $W(\nu_s-\nu)$ is the spectral window function, centered at ν_s which is the setting of the spectrometer, if $I_0(\nu)$ is the incident intensity, and if $T(\nu)$ is the *true* transmission function, then the *observed* transmission curve $O(\nu_s)$ is given by

$$O(\nu_s)=k\int_0^\infty I_0(\nu)T(\nu)W(\nu_s-\nu)d\nu, \qquad (4)$$

where k is a normalizing constant having dimensions of reciprocal frequency. In practice, the integration must be carried out over the extent of the spectral window for which the luminosity is appreciable, but note especially that "appreciable" really means with reference to the integral of Eq. (4), not merely to the relative ordinate values of the window alone.

Figure 3 is intended to illustrate Eq. (4) for the absorption-edge problem for one position of the spectral window and for the case of $I_0(\nu)=$ constant. Although the spectrometer is set with the spectral window
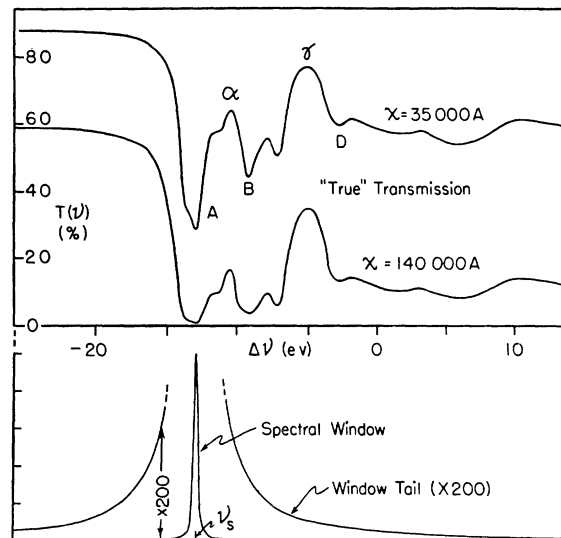

FIG. 3. "True" transmission curves, one for each of two absorber thicknesses, and a typical spectral window. The tails of the window are also shown plotted on an enlarged ordinate scale. The spectral window is pictured with its center ν_s at the A minimum in the transmission curves. The observed transmission curve $O(\nu_s)$ is obtained by placing ν_s successively at each of many different positions along the ν scale and by noting for each position the integral value as expressed mathematically in Eq. (4).

centered at ν_s, and although the spectral window may be relatively very narrow at half-maximum, nevertheless considerable intensity of other frequencies, $\nu_s \pm \Delta\nu$, leaks through the tails of the window.

The special feature of the absorption-edge problem is the enormous asymmetry of the true transmission function $T(\nu)$. It is evident that when the spectrometer is set somewhere in the low-transmission (high-absorption) region of the spectrum, as in Fig. 3, the leak-through of lower frequencies is greatly enhanced by the high transmission there. Furthermore, the enhancement in the observed transmission $O(\nu_s)$ is greater when the spectrometer is set at the A position in the curve than at, say, the B position. The detailed enhancements for each of the many settings of the spectrometer are such as partially to "wash out" the inherent minima (and maxima) in the true $T(\nu)$ curve. This means that, relative to the more or less flat part of the high-frequency region of the $T(\nu)$ curve (a region for which the thickness effect may be taken as negligible), the A and B valleys in the observed transmission are partially filled up.

Also, since the wash-out occurs most in the low-frequency part of the structure, the true frequency (or wavelength) position of the absorption edge,[9] and of A (the peak in Fig. 1, the valley in Fig. 3), is shifted slightly toward higher frequency. In principle, every other maximum or minimum is shifted also, but whether it is shifted to a higher or to a lower frequency depends upon the details of the curve and upon the actual thickness of the absorber.

So far, our explanation of the thickness effect has dealt with the case of a single thickness. The full stature of the effect looms as we increase the thickness, for by so doing we increase the effective asymmetry of the true transmission curve. As the absorber is made successively thicker, the transmission in the high-frequency region drops more rapidly than does the transmission in the low-frequency region. For example, we note from Fig. 3 that quadrupling the thickness of the 35×10^3 A absorber reduces the transmission at the position A by a factor of about 18 times as much as the reduction in the low-frequency region, and, of course, the relative contribution of the low-frequency leak-through is hugely increased. In principle, as x increases, the wash-out of structure becomes almost complete, the maximum slope in the $O(\nu_s)$ curve greatly decreases, and the observed absorption edge shifts markedly to higher frequencies. Fortunately, such overwhelming thicknesses are impractical, but, depending upon his desired accuracy, the investigator may easily run afoul of a too-thick absorber.[10]

The thickness effect may be opposed or aided by the use of an incident beam whose intensity function $I_0(\nu)$ varies significantly over the pertinent spectral region (i.e., the region of the window tails). For example, one may use as $I_0(\nu)$ the continuous spectrum near the high-frequency limit, or one may use the side of an intense emission line. The effect is aided in the former case and also in the latter case if the line is centered on the low-frequency side of the edge, but the effect is opposed if the line is centered on the high-frequency side of the edge, e.g., the Pd $L\alpha_1$ line in the present Cl K spectrum. In either event, of course, the asymmetry of $I_0(\nu)$ must be taken into account according to Eq. (4).

In the present work, the continuous spectrum from a platinum target[5] was used for all the curves represented here. This $I_0(\nu)$ spectrum was more or less flat. But, in order to demonstrate the effect of an asymmetric $I_0(\nu)$, the side of the Pd $L\alpha_1$ line was used for a few curves.[11] The relative frequency position of this Pd line is shown in Fig. 1.

SPECTRAL WINDOW SHAPE

If we knew completely the three functions in the integrand of Eq. (4), we could, at least in principle, compute the thickness effect. For example, $I_0(\nu)$ may be a known section of the continuous spectrum. A satisfactorily close approximation to $T(\nu)$ can be deduced from an observed $O(\nu_s)$ curve recorded with a thin absorber (after the curve has been corrected for the instrumental resolving power according to a new method[12]). Unfortunately, the window function $W(\nu_s - \nu)$, although it may be assumed to be symmetrical and constant in shape, remains unknown to within the required accuracy in the very important regions of the tails.

An attempt has been made to work backward, i.e., to deduce the window function $W(\nu_s - \nu)$, using the observed thickness effects as a starting point. The work is tedious and difficult, and we conclude that a reliable unambiguous window function is not deducible from the measurements at hand. However, from this work, we believe that the most probable window function of our two-crystal spectrometer in the $(1, +1)$ position has about the following characteristics: (1) it drops initially about as the Lorentzian, viz.,

$$W_L(\nu_s - \nu) = \frac{w^2}{w^2 + (\nu_s - \nu)^2}, \quad (5)$$

the true function, i.e., before the spectrometer has acted upon it.) Initially, as x increases, the magnitude of the slope of the curve $[\ln O(\nu_s)]$ vs x decreases if ν_s is at or near a deep minimum in the transmission curve, or it may increase if ν_s is at or near a sharp maximum in the curve. For some particular values of ν_s, $O(\nu_s)$ may show no thickness effect.

[11] The thickness effect was not known prior to the present work and the absorption curves reported by J. W. Trischka, Phys. Rev. **67**, 318 (1945), and by L. G. Parratt and E. L. Jossem, Phys. Rev. **97**, 916 (1955), were taken for intensity convenience with the Pd $L\alpha_1$ line as $I_0(\nu)$. The distortion so introduced is small in this case and is (at most) about twice as great as the experimental probable error.

[12] L. G. Parratt and C. F. Hempstead (to be published) and L. G. Parratt and J. O. Porteus (to be published).

---

[9] Often the frequency position of the edge is more or less arbitrarily taken as at the first inflection point in the absorption curve μ vs ν. It is also often taken, with less theoretical justification, as the first inflection point in the transmission curve.

[10] It is clear that the effect can be expressed as the deviation from linearity of the curve $[\ln O(\nu_s)]$ vs x for any given setting ν_s. (The curve of $[\ln T(\nu_s)]$ vs x is linear because $T(\nu_s)$ is defined as

where w is the half-width at half-maximum ($w \doteq 21$ seconds of arc, Bragg angle, reckoned by rotating only one crystal[13]), and follows this function for a distance equal to about w, then (2) it drops more rapidly, reaching approximately the square of a Lorentzian matched at the half-maximum, then less rapidly and crosses the Lorentzian at about $15w$, then (3) drops more and more slowly compared with the Lorentzian as $|\nu_s - \nu|$ continues to increase. The tail farther out than $100w$ is probably still very appreciable although out here we cannot conclude as to the slope, asymmetry[14,15] or other aspect of shape from the data at hand[16]; we can conclude only as to a "lumped" area. The fraction of the area of the experimental window beyond about $15w$ is roughly twice as great as the corresponding fraction for the Lorentzian model window.

It is possible, but not specifically required from this analysis, that an appreciable tail exists even at very large distances, at several hundred w, where the window has essentially diminished to spurious and thermal scattering.[17] At $|\nu_s - \nu|$ equal to about $300w$, the geometrical effect of the slits limiting the horizontal divergence of the beam in our two-crystal spectrometer no doubt causes a marked drop in the slope of the window

tails (essentially to zero slope), but with the data at hand such a "cutoff" was not discerned.[18] In practice, it is either this geometrical effect or the relative sensitivity of the detector (e.g., the channel discriminator in our detector) that bounds the spectral window, and also provides the practical limits of the integration in Eq. (4).

It was further concluded that in $O(\nu_A)$ the contribution from that part of the spectral window for all values of $\nu_A - \nu$ beyond $20w$ may be about 7% of the observed value for $x = 35 \times 10^3$ A, and may be as large as 80% for $x = 235 \times 10^3$ A.[19] These percentages can be deduced very roughly from the following relation:

$$\%_{Ox} = \left(\frac{T_{xA} - T_{Ac}}{T_{xl}} \right) \times 100,$$

where T_{xA} is the observed transmission at A for thickness x, T_{Ac} is the "observed" transmission at A extrapolated to zero thickness (from a curve similar to those shown in Fig. 2), and T_{xl} is the observed transmission on the low-absorption side of the absorption edge for thickness x. The large leak-through contributions give a pragmatic realization of the importance of the remote tails (beyond $20w$), a realization that the authors believe is afforded by no other calculations or experiment to date.

CONCLUSIONS

The "thickness effect" demonstrates that, for *accurate* absorption structure work, the optimum thickness of the absorber is much less than the value or values one calculates by maximizing the experimental precision in the measurements of intensities or absorption coefficients, or the respective differences or ratios thereof. The explanation of the effect lies in the role of the spectral window of the spectrometer. Because of the asymmetrical nature of an absorption edge, the remote tails of this window assume a great and heretofore unsuspected importance.

---

[13] This numerical value of w is the half-width at half-maximum of the (1, −1) curve at the wavelength of the chlorine K edge.

[14] The theory of diffraction of x-rays by crystals (Darwin-Ewald-Prins theory) predicts an asymmetrical diffraction pattern near the peak, the low-frequency side dropping somewhat more rapidly. Experimental confirmation of this type of asymmetry is afforded by the observed asymmetries of some $(n, -n)$ curves of the two-crystal spectrometer with nonidentical crystals, and by the recent neat demonstration by M. Renninger, Acta Cryst. 8, 597 (1955). Asymmetry near the peak, however, is of but little practical concern if the window is much narrower than any maxima or minima in the true spectrum.

[15] If the center of the geometrical slit pattern is not properly placed, and if the two effective slits are of nearly equal width, a very significant asymmetry is introduced in the window by the horizontal divergence in the incident beam. The vertical divergence also contributes to the asymmetry but is usually of little consequence [see, however, L. G. Parratt, Phys. Rev. 47, 882 (1935)].

[16] It should be noted that the tails of the diffraction pattern of a single crystal are not as high as for the two-crystal arrangement, and the thickness effect with a spectrometer using a single crystal, either plane or bent (focusing), would probably be somewhat less. We must be careful, therefore, in interpreting the numerical values of resolving power of instruments that have spectral windows of different shapes. See footnote 3.

[17] Fluorescent x radiation is also included in the window; in the present study the Ca K radiation from the first calcite crystal is by no means negligible in the remote tails of the two-crystal spectrometer. If the spectrometer is properly adjusted and operated and if a flat $I_0(\nu)$ beam is used, the (1,−1) curve gives a rather close representation of the spectral window to about $15w$. We have attempted to study the remote tail regions with such a curve. The difficulty is that we don't know how, in practice, to distinguish unambiguously the tail from the background.

[18] It is interesting to note that, with one horizontal slit set about 1/3 (or less) as wide as the other effective slit, two "cut-offs" on each side can be and have been observed in a (1, +1) curve if the curve is specially run by rotating the crystals but *not* the collimating slits. In such a run the center of the crystal diffraction pattern ν_s is progressively shifted with respect to the fixed center of the geometrical slit pattern, and as the crystal pattern crosses first the trapezoid shoulder and then the trapezoid edge (the edge corresponds in angular measure to the *maximum* horizontal divergence), the intensity of the observed (1, +1) curve first rather abruptly decreases and then becomes flat (zero).

[19] The authors are indebted to Mr. Darrell C. Kent for assisting in these calculations which were carried out by the laborious method of graphical integration.