APPENDIX A

Correction of Efficiency of Flow-Proportional Counter for X-ray Scattering

Suppose that an x-ray beam of initial intensity I_0 photons cm^{-2} sec^{-1} and cross sectional area A cm^2 traverses the flow proportional counter as shown in Fig. 1. Having passed a distance x into the counter gas its intensity is $I_0 w e^{-\rho\mu x}$. Now consider x-ray scattering from a volume element $A dx$. The scattered intensity is $\rho\mu_s A dx \; I_0 w e^{-\rho\mu x}$ photons sec^{-1}, where μ_s is the sum of the mass attenuation coefficients for coherent and incoherent scattering. The radiation escaping from the detector without being absorbed is then

$$dI_s = \rho\mu_s A dx I_0 w e^{-\rho\mu x} e^{-\rho\mu\epsilon} \quad (1.1)$$

where $e^{-\rho\mu\epsilon}$ is an attenuation factor representing an average over all directions of scatter. To a good enough approximation we may consider this attenuation factor to be independent of x. Integrating over x between limits 0 and l, the escaping scattered radiation is, in all,

$$I_s = (\mu_s/\mu)A I_0 w e^{-\rho\mu\epsilon}(1 - e^{-\rho\mu l}) \quad \text{photons sec}^{-1} \quad (1.2)$$

The absorbed radiation, on the other hand, is I: $= I_0 A w(1 - e^{-\rho\mu l})$ photons sec^{-1} so that the relative change in efficiency is

$$\frac{\Delta E}{E} = -\frac{I_s}{I_a} = -\frac{\mu_s}{\mu} e^{-\rho\mu\epsilon} \quad (1.3)$$

We must now decide upon a suitable choice for ϵ, which represents an average escape distance for scattered radiation. We note that if we express ϵ as some fraction of l, e.g., $\epsilon = \alpha l$, then $e^{-\rho\mu\epsilon} = [1 - (E/w)]^\alpha$ since, from Eq. (1), $e^{-\rho\mu l} = [1 - (E/w)]$. When E/w is small, results are obviously quite insensitive to the choice of α. Fortunately, when E/w is larger, μ_s/μ is generally small; the correction is then also small and need not be evaluated accurately. Consequently, the value chosen for α is not critical and we have taken $\alpha = 1/\sqrt{2}$ as a reasonable value based upon the geometry of our detector. We then have

$$\frac{\Delta E}{E} = -\frac{\mu_s}{\mu}\left(1 - \frac{E}{w}\right)^{1/\sqrt{2}} \quad (1.4)$$

More elaborate calculations indicate that errors introduced by use of this approximate formula are insignificant in terms of their influence on corrected values of efficiency.

APPENDIX B

Measurement of Dead Time

For the measurement of dead time we have used the following approach. When the dead time of the measuring system is τ, the true count rate I is related to the measured count rate I' by $I = I' (1 - I'\tau)^{-1}$ provided that $I'\tau \leq 0.05$. Then $I \approx I' (1 + I'\tau)$. Placing an absorber alternately in and out of the x-ray beam to measure its transmittance as a ratio of count rates, we find that the true transmittance T is related to the measured transmittance T' is related to the measured transmittance T' as follows.

$$T = \frac{I_1}{I_2} = \frac{I'_1(1 + I'_1\tau)}{I'_2(1 + I'_2\tau)} \approx \frac{I'_1}{I'_2}\{1 + (I'_1 - I'_2)\tau\} \quad (2.1)$$

i.e.,

$$T \approx T'\{1 + \tau\Delta I'\} \quad (2.2)$$

If we repeat the experiment using a different x-ray intensity, then

$$T \approx T''\{1 + \tau\Delta I''\} \quad (2.3)$$

Equating the two expressions for T, we obtain

$$\tau = \frac{T' - T''}{T''\Delta I'' - T'\Delta I'} \quad (2.4)$$

In practice we arrange for the two beam intensities to be in the approximate ratio 2:1. Each measurement of τ provides an experimental value for T, the true transmittance. After a number of measurements we have a reliable average value of T for the given absorber at a given photon energy, and thereafter dead time can be measured with one beam intensity alone using Eq. (2.2).

Statistical errors in counting generally give rise to a relative error of 10 to 15 % in τ. Since $I = I'(1 + I'\tau)$. we have $dI/I \approx I'\Delta\tau$. When $\tau \approx 1$ μsec, the relative error in corrected count rate is 0.1 % when $C \approx 10^4$ counts/sec, and errors in the ratio of two count rates are less. For this reason we have operated in most of our experiments with count rates no higher than 1.5×10^4 counts/sec.

Integral Reflection Coefficient of X-ray Spectrometer Crystals

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Analyzing crystals used in x-ray spectrometers have widely varying diffraction efficiencies. When employed in x-ray fluorescence analysis, the parameter which defines the efficiency is the integral reflection coefficient. This parameter has been measured using a single crystal spectrometer, as a function of wavelength, for a number of crystals com-

monly used. A recent adaptation of an existing diffraction theory is shown to make possible the calculation of integral reflection coefficients which agree with measured values.

Index Headings: Crystals; Diffraction efficiency; Instrumentation; X-ray; Optics; X-ray diffraction; X-ray fluorescence; X-ray spectrometers.

INTRODUCTION

The diffraction efficiency of crystals is an important parameter in x-ray spectroscopy when used for fluorescence analysis, plasma diagnostics, and ion collision studies. This diffraction efficiency, along with source brightness and detector efficiency, determines the intensity and therefore the time required to accumulate the number of counts necessary for the desired statistical precision. The diffraction parameter by which different crystals should be compared when being used in conventional flat crystal x-ray optics (or curved crystal optics used with an extended source and a slit) is the integral reflection coefficient.[1] It is the purpose of this communication to describe how these measurements can be made using a conventional single crystal x-ray fluorescence spectrometer (where the incident radiation is not highly parallel) and to illustrate how the diffraction efficiency of several commonly used crystals varies over their normal wavelength range. Further, a few examples will be given showing how these empirical values compare with some calculations for real crystals made using a new adaptation of an existing theory.[2]

I. BACKGROUND

Historically, crystal parameters have been measured on a double crystal spectrometer, a rather specialized instrument not available in many laboratories. Experimental details of the use of this instrument are not given here because there have been reported frequently.[3, 4]

The *crystal* parameters of interest are the angular breadth at half maximum, W, the peak diffraction coefficient, P, as a percentage of the incident intensity, and the integral reflection coefficient, R, the area under this curve. Fig. 1a shows a typical rocking curve with the three parameters identified.[3] Because the P value is unitless, the units of R are in angular measure, commonly radians.

The common single crystal spectrometer cannot produce parallel radiation because of the divergence allowed by the collimator (or slit in a curved crystal instrument). Strictly speaking it also cannot provide monochromatic radiation incident on the crystal. The latter difficulty can be minimized by using characteristic lines which are nearly monochromatic. The divergence allowed by the collimator will affect the measured line width which will be the convolution of the collimator divergence angle and the crystal rocking curve. Since the collimator divergence will be much larger in most cases than the crystal rocking curve, it is impractical to attempt to unfold the line width to determine the rocking curve breadth. But, because the integral reflection coefficient must remain constant,[5] the increase in line width will be accompanied by a decrease in peak line intensity, as illustrated in Fig. 1b. Some recent measurements[6] using a variety of collimators confirm the validity of this premise.

The data reported in this paper are *single crystal R* values, differing from those which would be measured on a double crystal instrument because the beam incident on the crystal of interest in the latter device is partially polarized by the first crystal. It is not a trivial problem to adjust the double crystal values for this effect because most real crystals fall in the region intermediate between the ideally mosaic and the perfect crystal theories. Even for graphite "crystals" which have been assumed to approach the ideally mosaic type, observations of polarization have been made[7] which are inconsistent with ideally mosaic behavior. For quantitative absolute measurements with a single crystal spectrometer, such as we have reported previously,[8] the use of integral reflection coefficients deter-
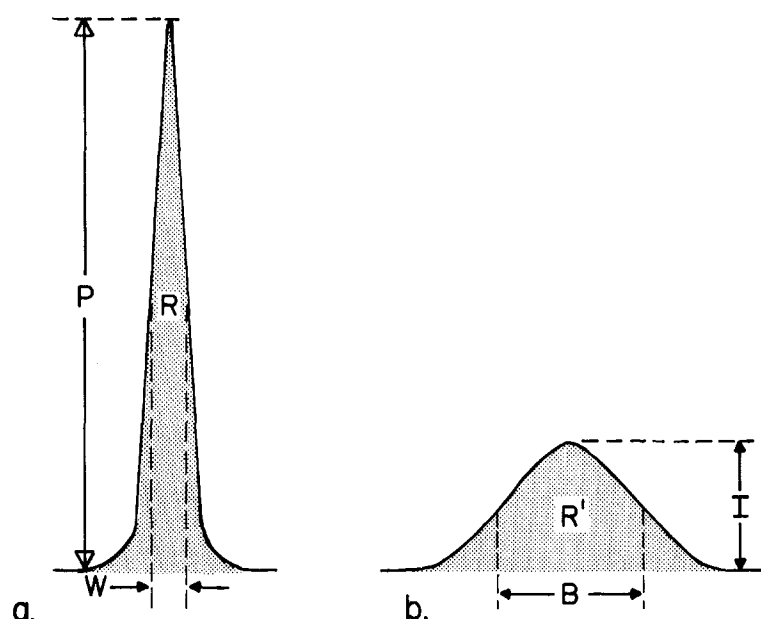

Fig. 1. a, diffraction rocking curve of a crystal: P is the peak diffraction coefficient, W is the full width at half-maximum of the rocking curve, and R is the integral reflection coefficient. b, line shape from part a as it would be measured in a typical single crystal spectrometer: line intensity (I) is *not* equal to P, line width (B) is *not* equal to W, but R' is exactly equal to R.

mined on a single crystal instrument eliminates the uncertainty associated with making polarization corrections to double crystal values.

A caveat must be given to the reader at this point. These single crystal R values were measured using fluorescer sources which emit unpolarized radiation and are appropriate *only* for use with similarly unpolarized sources, as in x-ray fluorescence analysis. Some x-ray sources may be polarized, and it must be understood that the values reported here will not be accurate for these situations unless some adjustment is made for the polarization.

II. EXPERIMENTAL

The flat single crystal spectrometer used for the measurements reported here is a standard Philips vacuum spectrograph equipped with a 0.0127-cm $\times$ 10-cm primary collimator. Fluorescers were excited by W- or Cr-target x-ray tubes operated at power levels consistent with the counting rates required. One of the crystal holders on the two-crystal changer was removed in order to make it possible to measure the incident beam. Gas proportional counters were used: a sealed, Xe-filled, mica-window model for short wavelengths, and a flow detector using P-10 gas and having a 100 μg/cm² stretched polypropylene window for long wavelengths. Conventional single channel counting electronics were combined with a multichannel analyzer, thus providing both digital and analog readout simultaneously. The geometry is shown schematically in Fig. 2.

The experimental procedure was as follows. With the crystal translated out of the beam, the spectrometer was set at 0°2θ and x-ray film was exposed in front of and behind the detector to insure that the entire beam was being measured. The x-ray generator was adjusted so that the counting rate (with the PHA set on integral, discriminating against only the electronic noise) was about 13 000 counts/sec. The dead time of the system was 3 μ sec; thus, the dead time involved in any measurement was no more than 4% and could be accurately corrected using the linear approximation. The primary beam was then recorded on the multichannel analyzer and on the single channel scaler (with appropriate settings of the PHA). The crystal was then translated into diffracting position and the appropriate 2θ range scanned to include Kα and Kβ. From this measurement, assuming that the diffraction efficiency of the crystal does not change over the small wavelength interval between these two lines, the fraction of the primary beam which is Kα can be determined. It is a
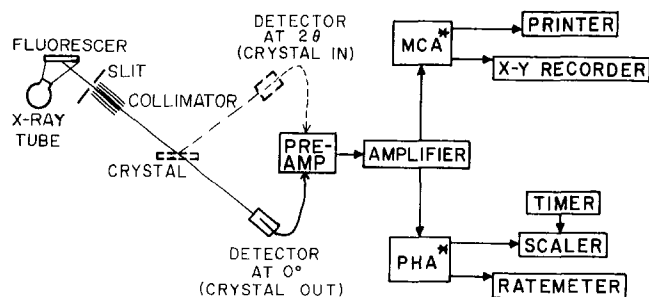

FIG. 2. Schematic of the experimental arrangement for measuring single crystal integral reflection coefficients. MCA = multichannel analyzer; PHA = single channel pulse height analyzer.

TABLE I. Integral reflection coefficient (in units of 10⁻⁵ Radians).[a]

Fluorescer	λ (Å)	LiF (220)	LiF (200)	Graphite	PET	ADP	Mica	KAP
Sn	0.492	13	32					
Ag	0.561	15	34					
Mo	0.711	15	35					
Zr	0.787	15	38					
Br	1.041	14	39					
Ge	1.255	13	38					
Zn	1.436	12	38					
Cu	1.542		36	220				
Ni	1.659	11	34				2.8	
Fe	1.937	11	31	160	27		2.7	
Cr	2.291	13	30	150				
V	2.505						2.6	
Ti	2.750		25	120	22	5.2	2.6	7.1
Ca	3.360		35	71			2.8	5.1
K	3.744		62		16	3.7	2.6	6.6
Cl	4.729			49			2.7	7.8
S	5.373			59	11	3.6	2.5	8.2
P	6.155			77			2.1	8.2
Si	7.126				13	3.2	2.9	8.2
Al	8.339					3.5	2.1	7.9
Mg	9.888					5.0		6.6
Na	11.91							5.2
Ni(L)	14.56							4.2
F	18.31							4.5

[a] PET = pentaerythritol; ADP = ammonium dihydrogen phosphate; KAP = potassium acid phthalate.

simple matter, then, to integrate the diffracted Kα line over the angular range of its diffraction profile and divide by the intensity of the Kα in the primary beam to obtain the integral reflection coefficient.

III. RESULTS AND DISCUSSION

The integral reflection coefficients of seven crystals are listed in Table I and shown plotted against wavelength in Fig. 3. It is estimated that these data are accurate to approximately ±10%. The dashed portions of the curves in Fig. 3 represent regions of larger uncertainty near absorption edges where data are sparse. The figure illustrates two different types of curves. The decrease in integral reflection coefficient for the two LiF curves at short wavelength is significantly different from the rest; the difference results from the inhomogeneity of the dislocation density in these abraded and etched crystals. More will be said about this later. All the curves show increasing R values at long wavelength except KAP and mica. This is not a real difference because the latter two curves would increase if data were given at a long enough wavelength (see Fig. 4 and Table I for KAP).

Data were taken for two (220) LiF crystals at different times. One crystal was prepared at the Naval Research Laboratory by being sawed from a block of LiF, abraded and etched; the other was a commercial crystal prepared elsewhere, presumably in the same way. The integral reflection coefficients of the two crystals were identical although it had been expected that there might be significant differences. The identical results from the two crystals indicate that the quality of "spectrometer grade" LiF is quite consistent. These results also suggest that the abrading and etching procedure is not difficult to reproduce. All
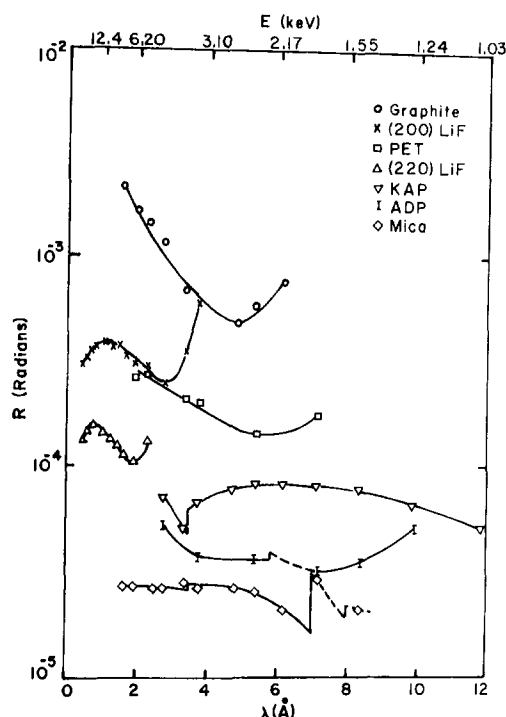
Fig. 3. Integral reflection coefficients, as a function of wavelength for seven commonly used crystals. (Data actually available for KAP to 18 Å; see Fig. 4.)
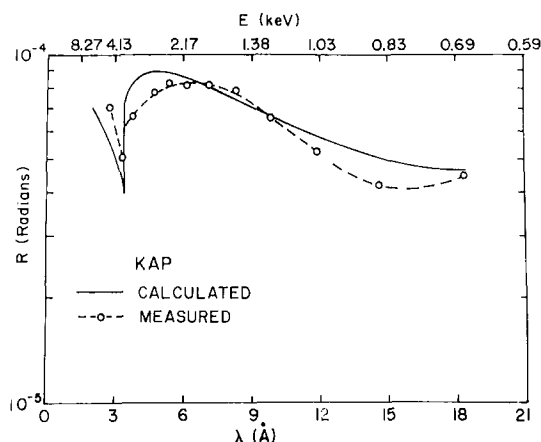

Fig. 4. Comparison of measured integral reflection coefficients for KAP with a calculation made according to Ref. 3.

of this is not intended to imply that all crystals will show such agreement; the values reported here should be considered typical both in magnitude and in variation with wavelength.

Some of our experimental measurements have been compared on an absolute basis with calculations according to a scheme devised by Brown et al.[2] These comparisons are illustrated in Figs. 4 to 6. In these figures the data points are taken from Table I and the curves are the results of the calculations. A description of these calculations is beyond the scope of this paper, but it should be mentioned that the major parameters required are the mosaic block size and the angular tilt between blocks. The reliability of the theory can be seen in the striking agreement between measurement and calculation for relatively perfect KAP (Fig. 4). It is interesting to note that the shape of the dis-

continuity at the K K edge was considered unreliable (suspected of being due to experimental error larger than usual near the edge) until it was confirmed by the calculation. The observed shape could be ascribed to anomalous scattering in this wavelength range. Similarly, the agreement between measurement and the new calculation for two different graphite crystals is quite good, as shown in Fig. 5. The lowest curve in the figure (crystal 1) is for the crystal listed in Table I; the data points for the other experimental curve represent a graphite crystal with a broader rocking curve due to larger angular tilt between mosaic blocks. Graphite is considered to be highly imperfect,[3] as is demonstrated by the similarity in shape between the measured curves and that which would be calculated from the ideally mosaic theory. However, the absolute
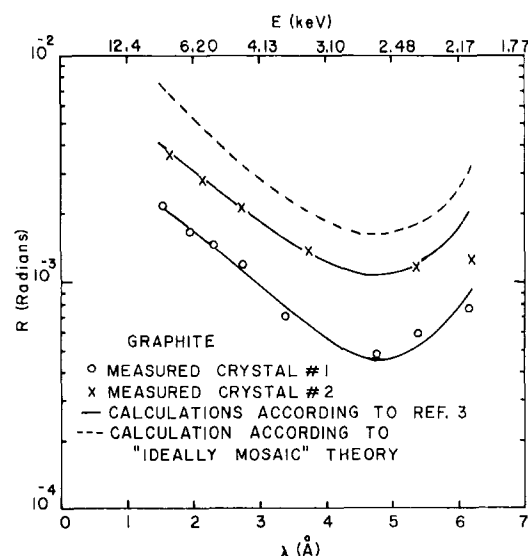

Fig. 5. Comparison of measured integral reflection coefficients for graphite with calculation according to Ref. 3 and according to the "ideally" mosaic theory. Crystal 1 has a rocking curve breadth of $\sim$0.4° while crystal 2 is $\sim$0.5°.
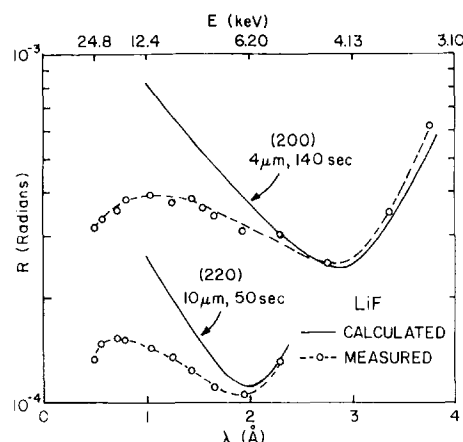

Fig. 6. Comparison of measured integral reflection coefficients of abraded and etched (200) and (220) LiF with calculations according to Ref. 3. The parameters listed for each calculation are the mosaic block size (in μm) and the mosaic block tilt (in seconds of arc). At short wavelength both crystals show a trend toward diffraction from more perfect regions of the crystal (larger block size, smaller misorientation). Not shown are the calculated curve for the perfect crystal case, which would be off the bottom of the graph, and the ideally mosaic case, which would be off the top.

magnitude of the measured values are lower than the mosaic theory predicts, thus demonstrating that the crystals are not "ideally" mosaic.

For the LiF case, comparison between the theory of Brown et al. and our measurements is more difficult. Both the (200) and (220) LiF crystals had been abraded and etched, a treatment commonly used for alkali halides to increase their diffraction efficiency.[9] This treatment introduces a high density of dislocations extending perhaps 50 μm below the surface; the longer wavelengths are diffracted entirely within this surface layer and, as shown in Fig. 6, the experimental points agree well with the calculations in this region. The more penetrating short wavelengths see both the surface and the more perfect bulk crystal below the abraded layer, in different proportion for different wavelengths. Thus the calculations diverge from the measurements toward short wavelengths because the parameters used in the calculations apply only to the abraded layer. No one set of parameters can satisfy the requirements of the short wavelength region because of the way the penetrating power varies with wavelength.

IV. CONCLUSION

The integral reflection coefficient of crystals to be used in x-ray fluorescence spectrometers can be measured in a single crystal instrument in a very straightforward manner. Values obtained do not suffer from the uncertainty asso-ciated with making a polarization correction to double crystal data. Reported here are single crystal integral reflection coefficients for a variety of crystals commonly used in x-ray spectrometers. Comparison of measurements with a reasonably sophisticated theory of crystal diffraction shows good agreement when the appropriate parameters necessary for the calculation are available.

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Identification of Oat Cultivars by Fluorescence Spectroscopy*

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A fluorescence spectrograph that operates in a reflective mode to identify oat cultivars is discussed. The wavelength of the exciting energy is 2400 Å, and the wavelength of the emission energy varies between 3000 and 5000 Å. Three peak and two valley points were identified and correlated with the different cultivars. A canonical analysis performed on various samples taken from six cultivars showed that they could be separated on the first two axes.
Index Headings: Fluorescence; Instrumentation, fluorescence spectroscopy

INTRODUCTION

Cultivars within a crop possess qualitative and quantitative differences which determine their market value. Plant breeders, seed lot operators, seed dealers, and farmers need a quick, objective, and reliable identification means to ensure that the variety grown is that intended. Food processors must also prevent the mixing of different cultivars. The rationale for exploring the technique reported here and its application to taxonomy were discussed by Baum and Brach.[1] This paper is concerned with aspects of oat fluorescence and use of a new method for varietal identification.

Finkner et al.[2] reported a varietal difference of fluorescence in oats. Morrison[3] investigated a method where fluorescent off-type seeds were picked from registered samples of nonfluorescent oats. Menke et al.[4] and Singh et al.[5] used a protein electrophoresis method to identify varieties. Crisp and Wrigley[6] used a phenol test for checking varietal purity and identity of cereal grain. Baum and Lefkovitch[7, 8] described a statistical model for oat cultivar classification. These techniques require that the sample be made into a solution or evaluated morphologically by visual inspection under a microscope, and they require a high degree of skill.

Brach[9] illustrated the differences in optical properties of cultivars for remote sensing measurements. Different species such as wheat, barley, and rye (Fig. 1, C, E, G) were identified by differences in amplitude at several wave-