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HIGH SPATIAL RESOLUTION

in X-RAY FLUORESCENCE

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NTRODUCTION

During the past eight years or so there has been growing interest in ısing a polarized x-ray source in energy dispersive x-ray fluorescence pectrometers(1,2,3,4). The effect is to annihilate the source x rays efore they scatter into the detector, thus significantly increasing the ignal to noise ratio.

Both characteristic or Bremsstrahlung radiation can be polarized by 0° scattering from crystals (Bragg angle = 45°) or from amorphous materials espectively. This 90° polarizing scatter event greatly reduces the npolarized source radiation. In an effort to regain some intensity use is ade of concave surfaces to utilize a manifold of beams (5,6,7). The case f a Johann polarizer has been discussed (8,9,10). The Johansson geometry 11) has been ignored because it is a highly focussed geometry. Sample omogeneity would thus be a problem. However, interest has now arisen oncerning the measurement of sample inhomogeneities (12) and the Johansson evice may find a new application. It should be mentioned that while it is ot necessary to polarize the x rays to use Johansson geometry, the olarizing geometry does offer the greatest distance between the x-ray ource and the sample. This may be important to the design of a functional nstrument. This paper is an effort to explore some of the potentials and roblems of using Johansson geometry in an EDXRF spectrometer.

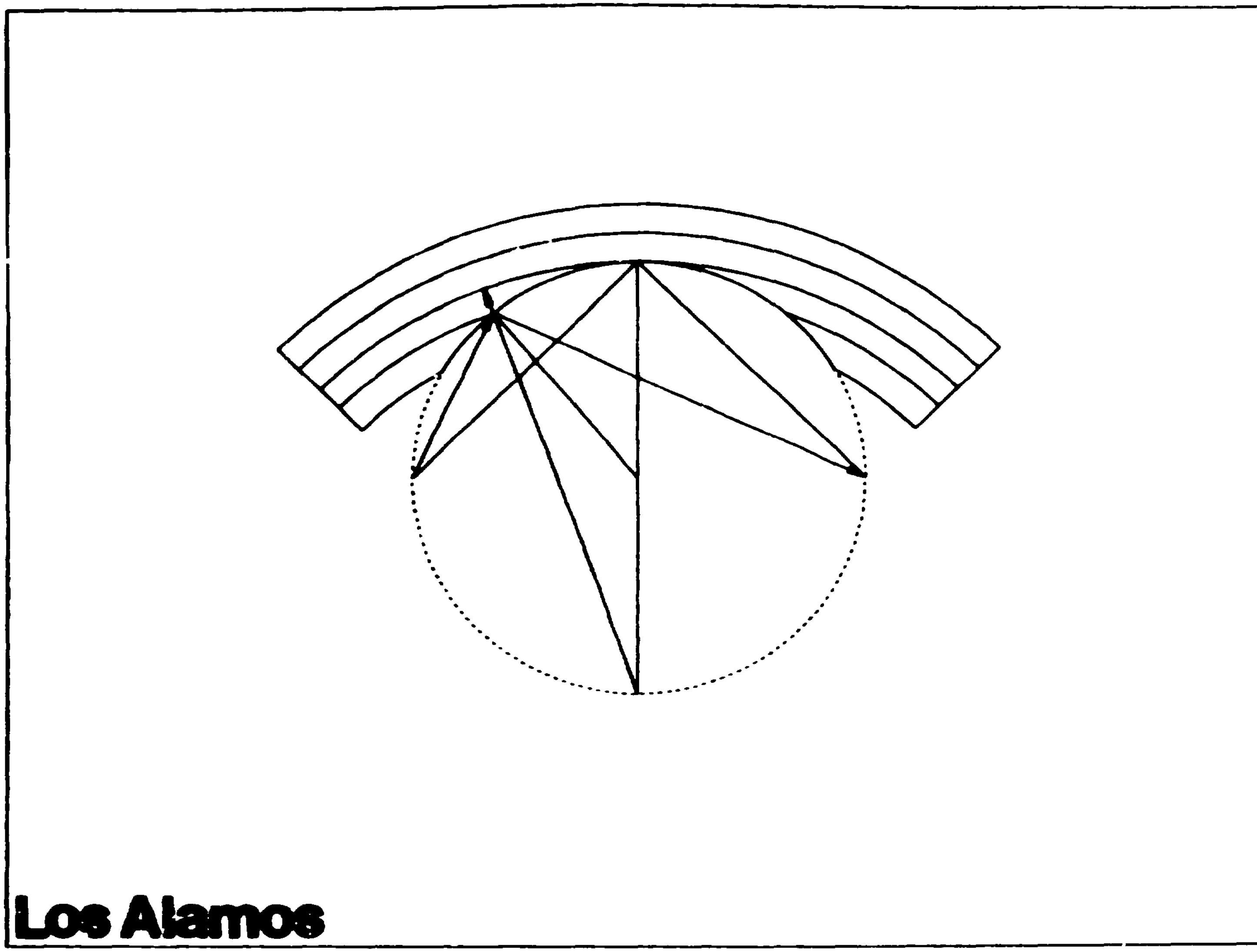
The kinematic theory of x-ray diffraction is used with a mosaic model f an imperfect crystal. The parameters inherent in the mosaic model are uch that the results presented herein are more retrodictive than redictive. The results point more toward potentialities than a specific xperiment. It should be noted however, that the mosaic parameters can be easured with a little effort (13).

Finally once the diffraction line shape, or intensity profile, on the ample is determined, the signal across various concentration gradients will e determined to a first approximation.

EOMETRY

The schematic geometry is shown in Fig. 1. The crystal is first ground o a radius R and then bent to a radius of 2R. This crystal then sits on he (conceptual) Rowland circle of radius R defined by the centers of the ource, S, and analyte, A, and the point O. S and A are on a diameter for

EAB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e case discussed herein but when used as spectrometer, S and A need only symmetrically positioned.

Every ray r_o from S to the ground portion of the crystal has a Θ_B = ° and the angle SPA is always 90° insuring the aspects of diffraction and larization.

A weighting factor, $\sin \Theta_B / r_o^2$ is also desired. The dot product of r_o th the plane normal, n, (a unit vector) gives $r_o \sin \Theta_B$ and calculation ves

$$\sin \Theta / r_o^2 = [\, R\cos \xi + R\sin \xi + \sigma(\cos \xi - \sin \xi)/\sqrt{2}] /$$

$$[2r_I^2 + \sigma^2\ 2R_I^2 \sin 2\xi + 2R\sigma(\cos \xi - \sin \xi - 1)/\sqrt{2}]^{3/2} \qquad (1)$$

The last geometric consideration of concern is, where on the sample is e diffraction line, from the ds region about s, centered? For the hnsson case it is always at z = 0.

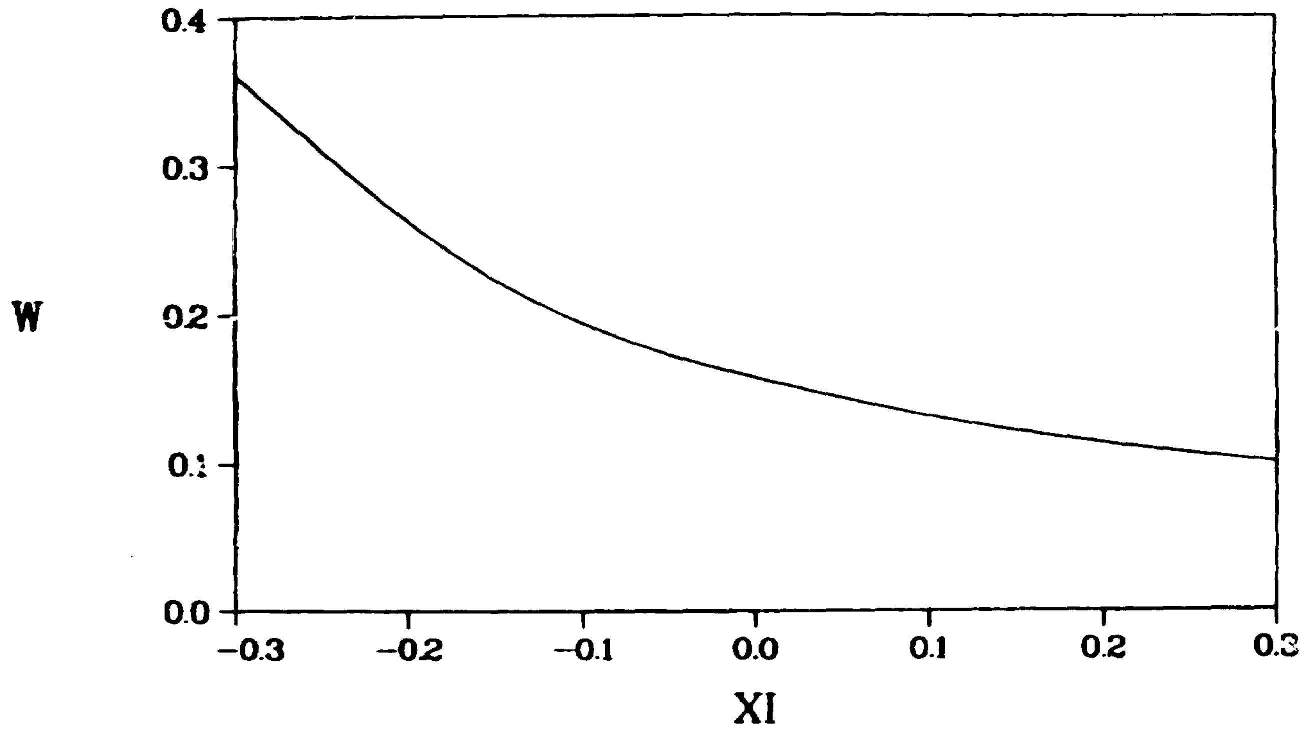
TENSITY PROFILES

In this section I wish to present the intensity profiles for the hansson and Johann (for comparison) polarizers. These profiles should be perimentally observable (e.g. by replacing the analyte by a piece of otographic film). Comparison of the experimental profile with that lculated here offers one test of the model.

If the source is finite in extent, each scattering point P will be thed by photons with a small but finite range of incidence angles. These n interact with a number of mosaic blocks on the arc length ds. The saic structure will broaden the focus at A by some small amount. It is sired to know just how much broadening there will be and to know the tensity profile along the line OA and is extension.

Let radiation of source intensity I_o be incident on the crystal with an gle of incidence Θ (measured between the tangent to the crystallographic ane and the direction of incident radiation r_o). The incident radiation s a normalized distribution function in y, D(y,s), where $y = \Theta - \Theta_B$ and s $2R\xi$, and a weight of $\sin \Theta / r_o^2$. The radiation is pictured as countering many mosaic blocks along the interval ds. The mosaic blocks ve a normalized distribution function $W(\Delta)$ over Δ, the angle between the rface of the microscopic block and the macroscopic crystallographic plane. ch mosaic block is perfect and has a reflectivity of $P_H(y)$. The flectivity from a ds region centered on s is

$$d\sigma(y,s) = I_o \sin \Theta / r_o^2\ D(y,s)\ dy\ ds \int P_H(y-\Delta)\ W(\Delta)\ d\Delta. \qquad (2)$$



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Now I assume that the absorption and extinction by the crystal are ligible so that $d\sigma(y,s)$ is the line shape of the diffraction line caused the mosaic blocks in a ds neighborhood about s (13). $D(y,s)$ can be taken be square wave in shape and broad compared to $W(y)$. Since the P_H ction is generally quite narrow compared to W, the Δ integration yields thout concern of the shape of P_H)

$$d\sigma(y,s)=I_o \sin\Theta / r_o^2 \, W(y)\, R_H \, ds\, dy \qquad (3)$$

re R_H is the area under $P_H(y)$. Eqn. 3 is to be evaluated numerically.

At the sample, y can be related to z by $y = z/r_d$. (Throughout this er the sample surface is assumed to be normal to r_d. This introduces a ll error in the profiles presented.) Thus z is to be fixed and the erical integration over s can be performed.

Parameter values used throughout are R=1.5 cm, η=0.001 rad and -)1$\leq\xi\leq$0.001. These are just the values used in (10). The function $W(\Delta)$ taken to be a normalized Gaussian function of standard deviation η.

Johansson intensity profile is shown in Fig. 2. The shape is entially Gaussian with a FWHM of 0.0018 cm. Keep in mind that the FWHM nearly a linear function of R.

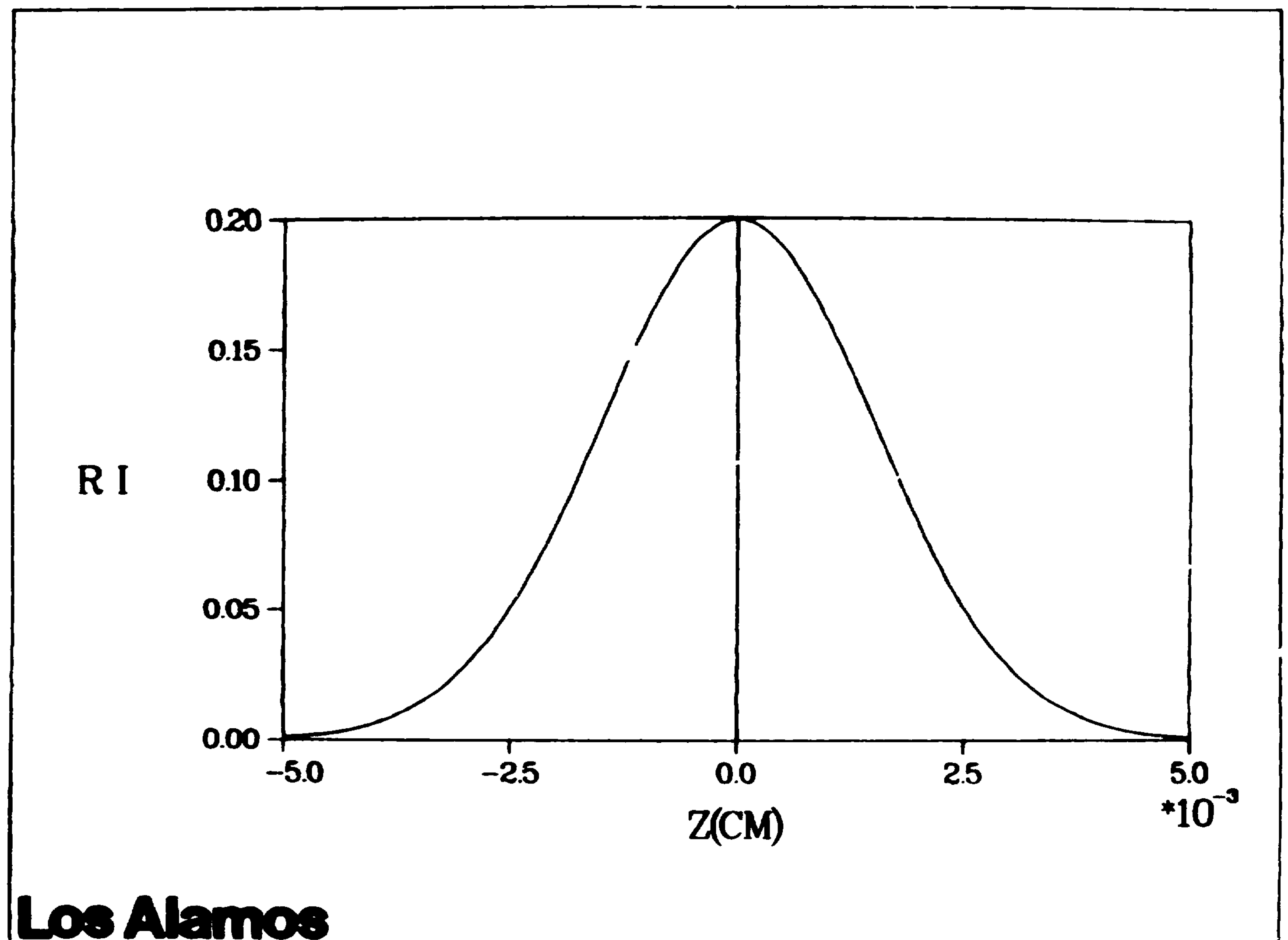
Although the geometry is different for the Johann case, $\sin\Theta / r_o^2$ is difficult to calculate and Eqns. (2) and (3) still hold. The new olem is that the center of the diffraction line on the sample, from the region about s, is itself a function of s. Once this is taken into ount the numerical integration is performed in like manner to the ansson case. The intensity profile is shown in Fig. 3. It is much ader than the Johansson case and noticeably asymmetric. The dashed line the figure portrays the "density" of the diffraction line centers. This first published by Johann (8).

NDARY EFFECTS

If the diffraction line has finite width, concentration gradients will be faithfully reproduced by gradients in the signal as the sample is ined. In particular, assuming the signal at a point, $S(z_o)$, to be oortional to the concentration of the analyte at that point, $c(z_o)$, times intensity at that point, $I(z_o)$ then

$$S(z_o) = k \int c(z)\, I(z-z_c)\, dz \qquad (4)$$

equation ignores the divergence of the diffraction beam and assumes centration is not a function of depth in the sample. No matrix effects



0.20
0.15
0.10
0.05
0.00
R I
-5.0
-2.5
0.0
2.5
5.0
*10^-3
Z(CM)
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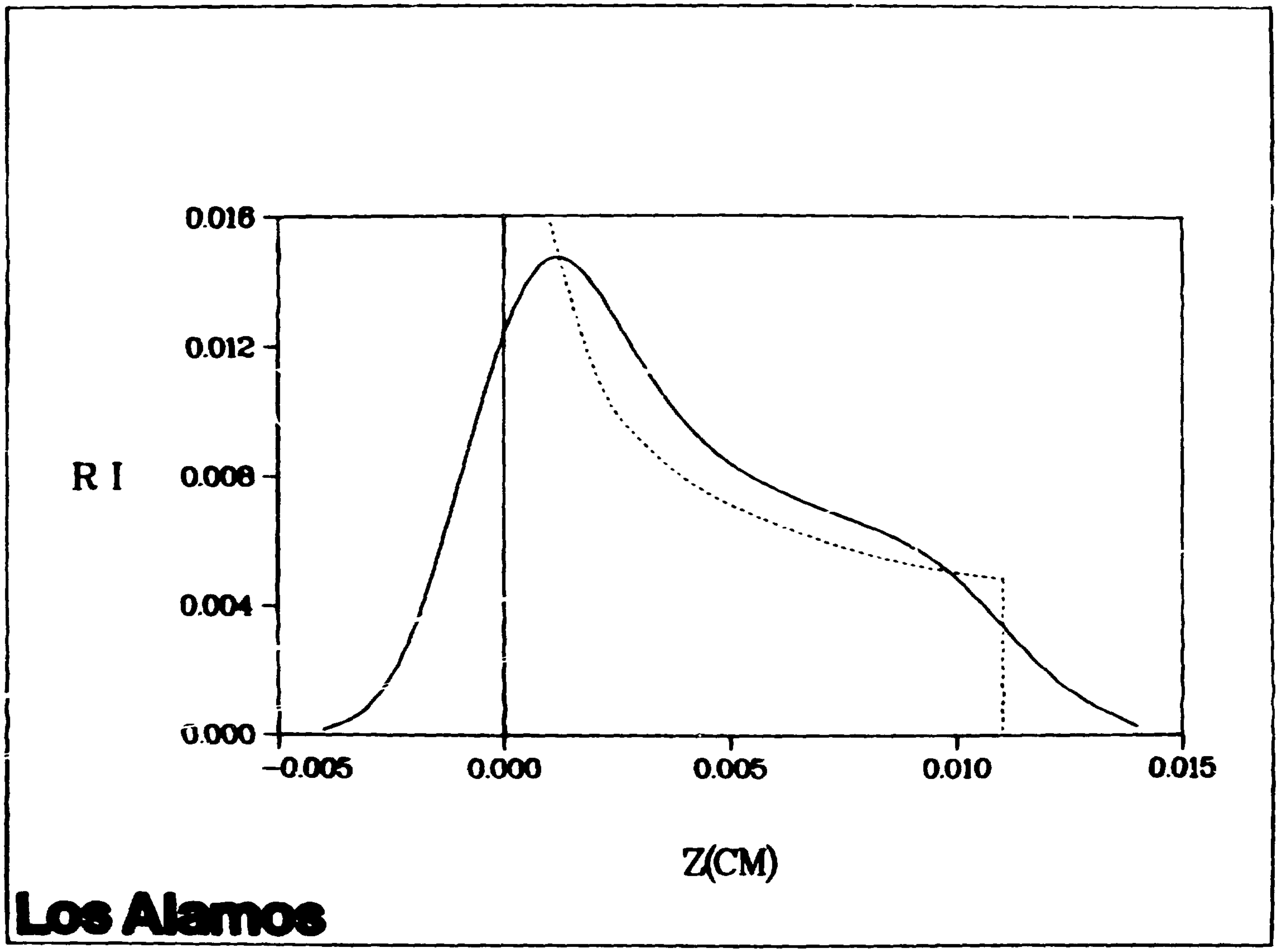
0.016
0.012
0.008
0.004
0.000
R I
-0.005
0.000
0.005
0.010
0.015
Z(CM)
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or interelement effects are considered although some very interesting effects and problems could likely be constructed.

I will consider four illustrative examples in concentration gradient; a) step function, b) linear gradient, c) exponential gradient and d) Gaussian gradient. The intensity function will be taken to be Gaussian, as was shown to be the case with the Johansson geometry.

With the parameters a=1 cm. and η=0.001 rad. graphs of these four cases are shown in Figs. 4-7 as S versus z. It is apparent that the broader the concentration gradient (relative to the intensity profile) the closer the signal maps the concentration. The presence of discontinuities of the concentration gradient also causes some relatively unfaithful mapping.

In general one will be faced with solving the deconvolution problem of eqn. (4) for c(z) given $S(z_o)$ and $I(z-z_o)$. This problem is, mathematically speaking, a Fredholm equation of the first kind. These problems are often ill-posed, ill-conditioned and underdetermined. Although numerous codes exist to solve these kinds of problems, the problems themselves are still nasty.

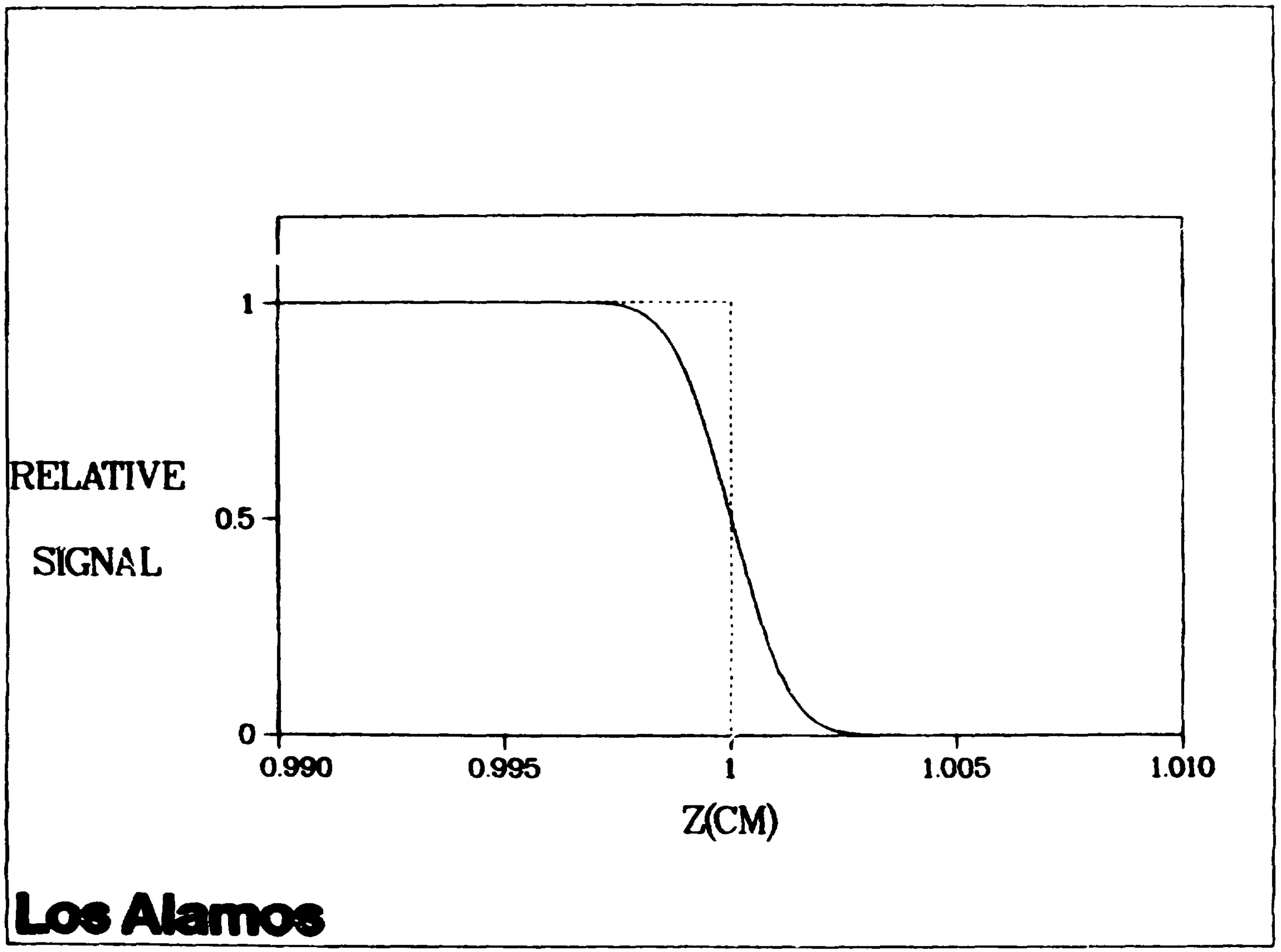
CONCLUSIONS

Johansson geometry is a focussing geometry as far as ray analysis is concerned. However, given the mosaic nature of real diffracting crystals, the intensity profile of a Johansson system may have appreciable intensity over 20 microns or so. Making the diffracting crystal as perfect as possible, in spite of the grinding and bending, will reduce the spot size. This will likely require annealing of the crystal. Making the system close coupled (R small) would also give smaller spot size but there would be greater divergence from the point of focus. In this case depth effects could be troublesome. There may also be trouble in mechanically getting the x-ray source, diffracting crystal, sample and detector all together in a close coupled system. Although there is no necessity in having the Bragg angle 45°, thus opening the door to many more diffracting crystals which may be more efficient for a given characteristic energy, the polarization geometry does offer the greatest distance between the source and sample.

Another problem lies in the fact that I have been discussing characteristic x rays only. Such a monochromatic source might not be very efficient for broad band analyses.

The collimated system reported by Nichols and Ryon (12) overcomes some of these problems but perhaps at some loss of total intensity due to the small collimator size.

With regard to boundary effects, I see no major problems in interpreting the data. While many interesting and difficult problems have been glossed over here, problems such as beam divergence, concentration depth effects matrix effects, etc. can all be incorporated into the simple theory reported here.


RELATIVE
SIGNAL
1
0.5
0
0.990
0.995
1
1.005
1.010
Z(CM)
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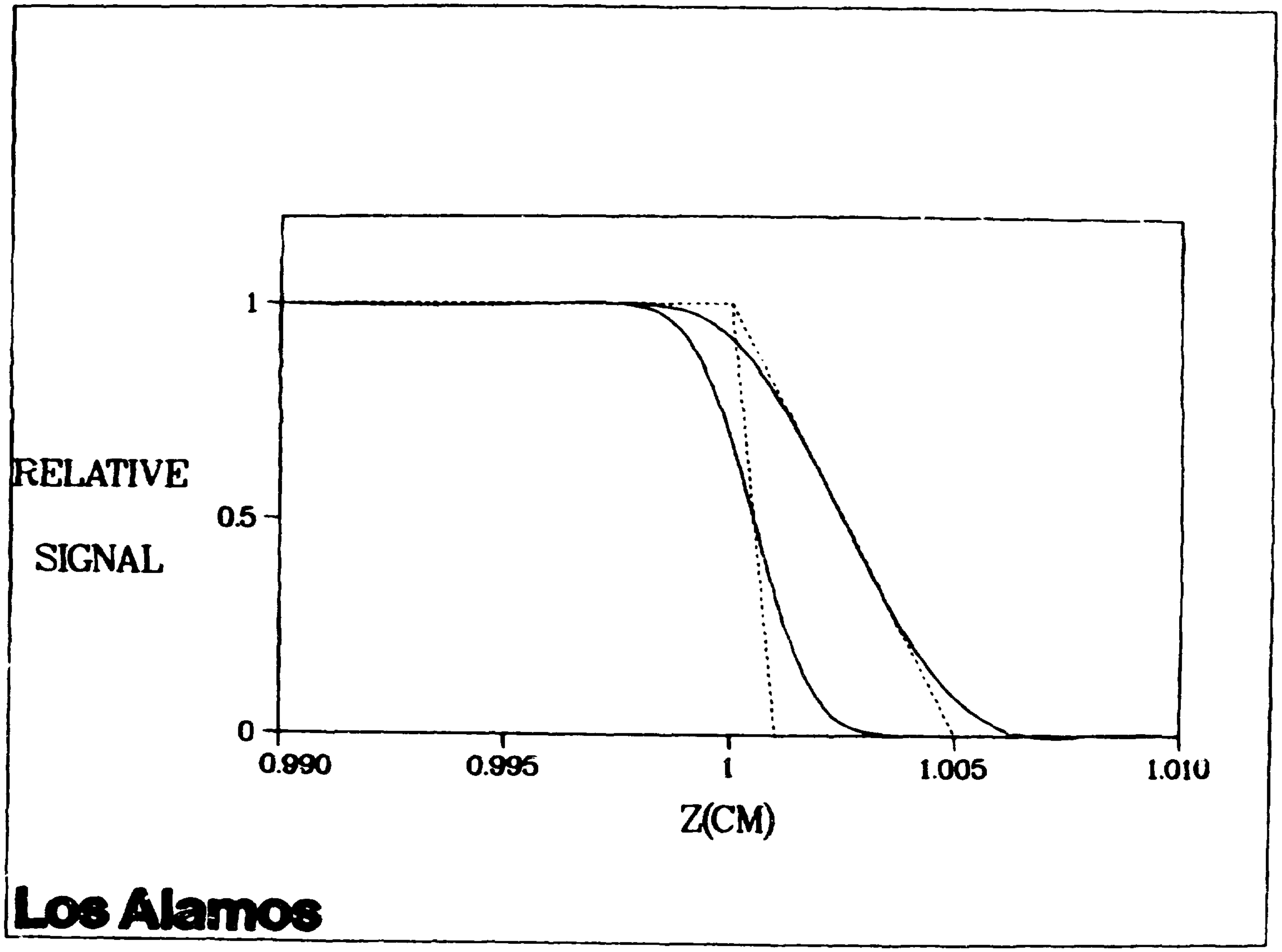
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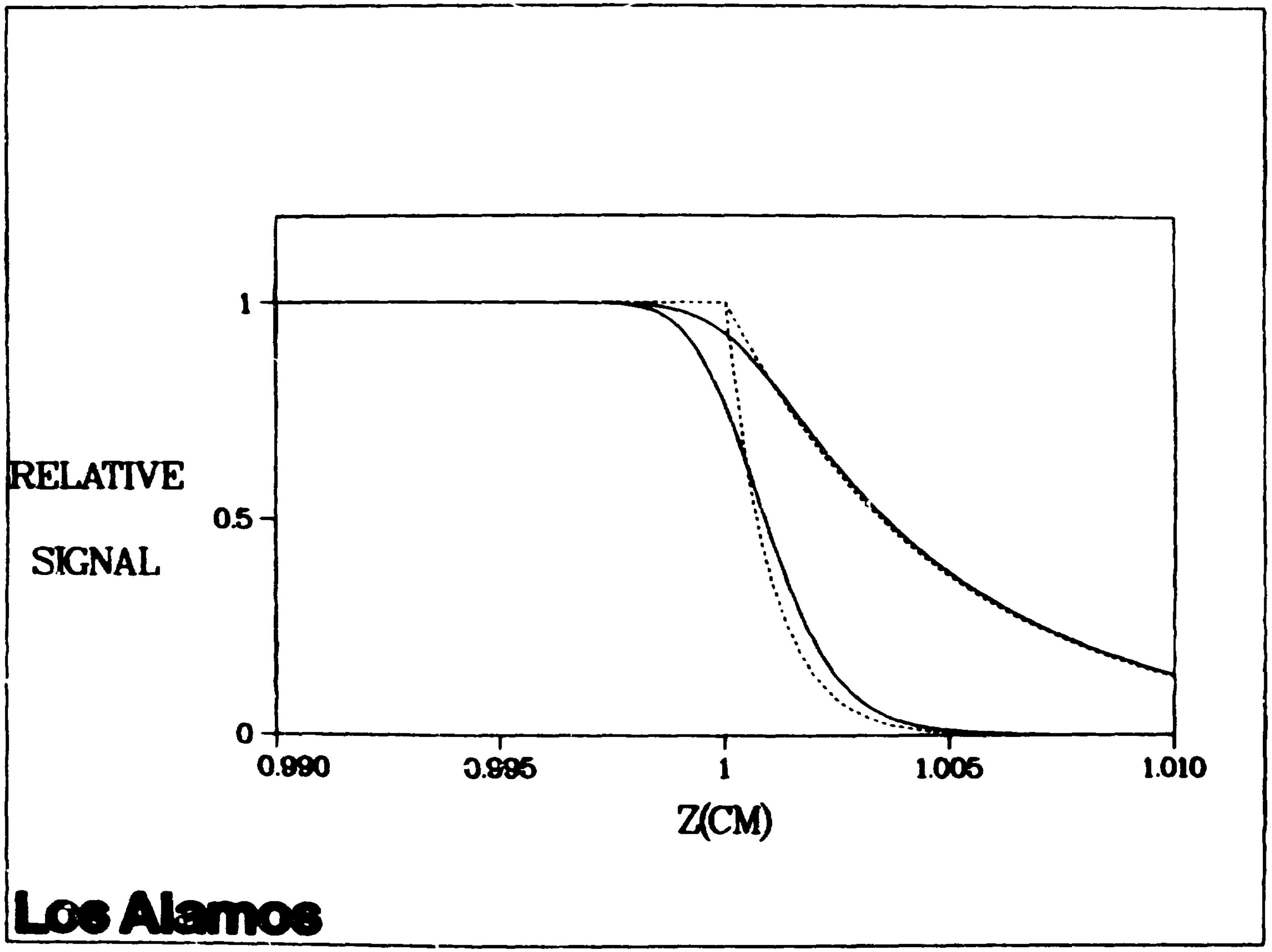
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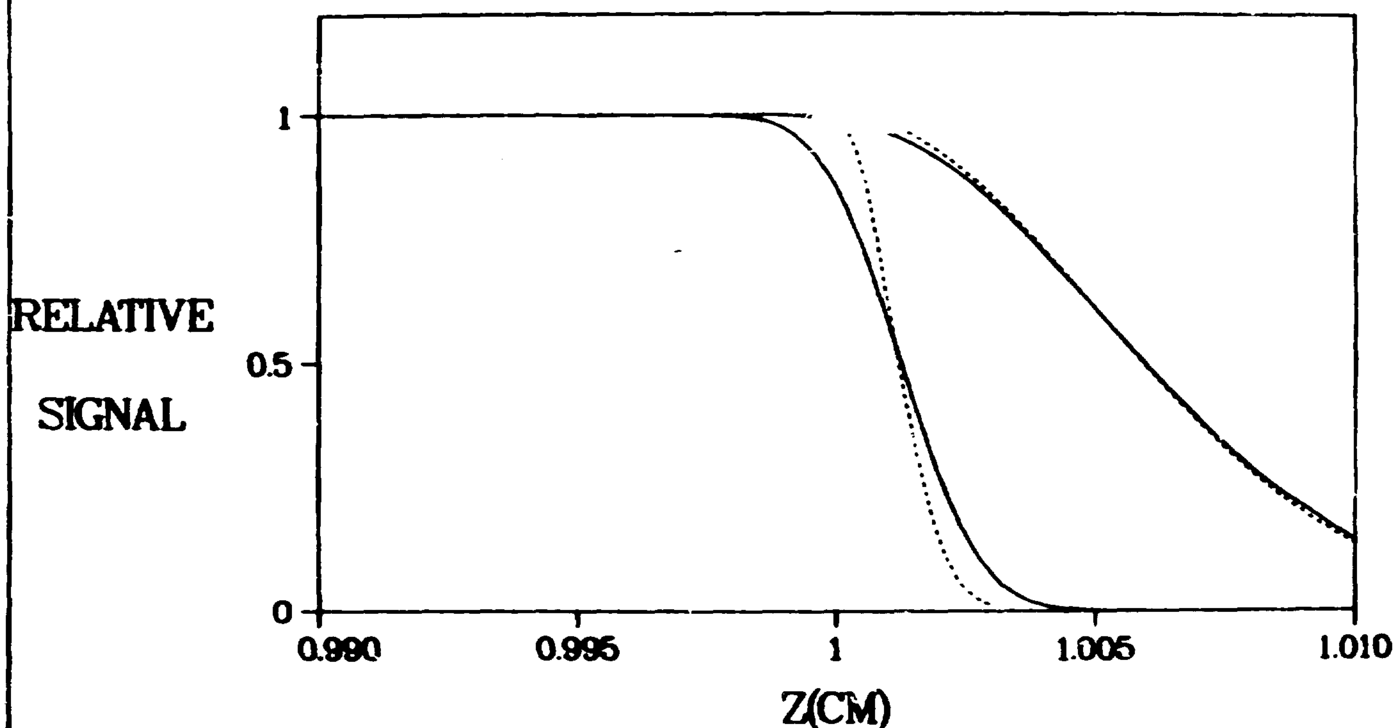

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