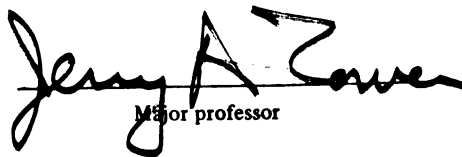


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X-RAY FLUORESCENCE SPECTROSCOPY OF CdTe SUBSTRATES

By

Daniel Ray Hines

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

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ABSTRACT

X-RAY FLUORESCENCE SPECTROSCOPY OF CdTe SUBSTRATES

By

Daniel Ray Hines

CdTe is a commonly used substrate material for epitaxial growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ which has gained tremendous attention in the infrared detector industry. It has been demonstrated that the properties of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ epilayer depends on defects and impurities present in the substrate. Therefore, the study of these defects and impurities in CdTe substrates is essential. We have performed x-ray fluorescence spectroscopy in conjunction with electron microscopy on CdTe substrates in order to study microchemical inhomogeneities. The sample preparation necessary for electron microscopy has been developed. Six CdTe substrates obtained through the Rockwell International Science Center were prepared and studied for stoichiometry and impurities. Te deposits and impurity deposits (especially Fe) are reported in addition to stoichiometric variations as large as 20%.

ACKNOWLEDGEMENTS

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INTRODUCTION

History of Infrared Detector Materials

CdTe is a commonly used substrate material for epitaxial growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ which has gained tremendous attention in the infrared detector industry. It has been demonstrated that the properties of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ epilayers depend on defects and impurities present in the substrate.^{1,2} Therefore, the study of these defects and impurities in CdTe substrates is essential. Let us put into perspective the role of II-VI semiconductors, namely CdTe and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, by first presenting a brief history of infrared detector materials.

Experimentalists in the 1800's first studied infrared radiation using thermocouples.³ Temperature measurements were recorded as a current change resulting from heating or cooling of a circuit junction made from two dissimilar metals. As materials research developed it was discovered that a number of intrinsic band gap semiconductors could also be used to study infrared radiation. In general, a semiconductor of energy band gap, E_g , is related to the longest wavelength, λ_{max} , that can be detected by

$$E_g = \frac{h c_o}{\lambda_{\text{max}}} \quad (1)$$

where h is Planck's constant and c_0 is the speed of light in a vacuum.⁴ For an intrinsic semiconductor, incident radiation of wavelength $\lambda_{\max}$ or less excites electrons from states near the top of the valence band into states near the bottom of the conduction band. Such excitations change the properties (i.e. electrical conductivity or photovoltage) of the material⁴. These changes can be recorded to measure the incident radiation.

The first intrinsic band gap materials used for infrared detector devices were elemental and compound semiconductors. These semiconductors have discrete band gaps and are well established in the 1-8 μm wavelength range as shown in Figure 1. The need soon arose, however, for infrared detectors that could be "tuned" to specific cut-off wavelengths and also cover the 8-12 μm wavelength range. It is possible to achieve such band gap tunability with ternary compounds where the concentration of the cations can be varied. One of the most promising ternary semiconductor materials for intrinsic infrared detectors is $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ which has an energy band gap that varies with concentration, x , as shown in Figure 2.

In terms of fabricating electro-optical device arrays, epitaxially grown $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ has shown certain advantages over bulk grown $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$. For instance, some geometries available with epilayer devices can avoid surface contamination problems inherent to bulk devices⁵. Also, for large scale production, small epilayers can be grown quite easily while small bulk pieces must be cut from large boules which is a slow process. However, there is

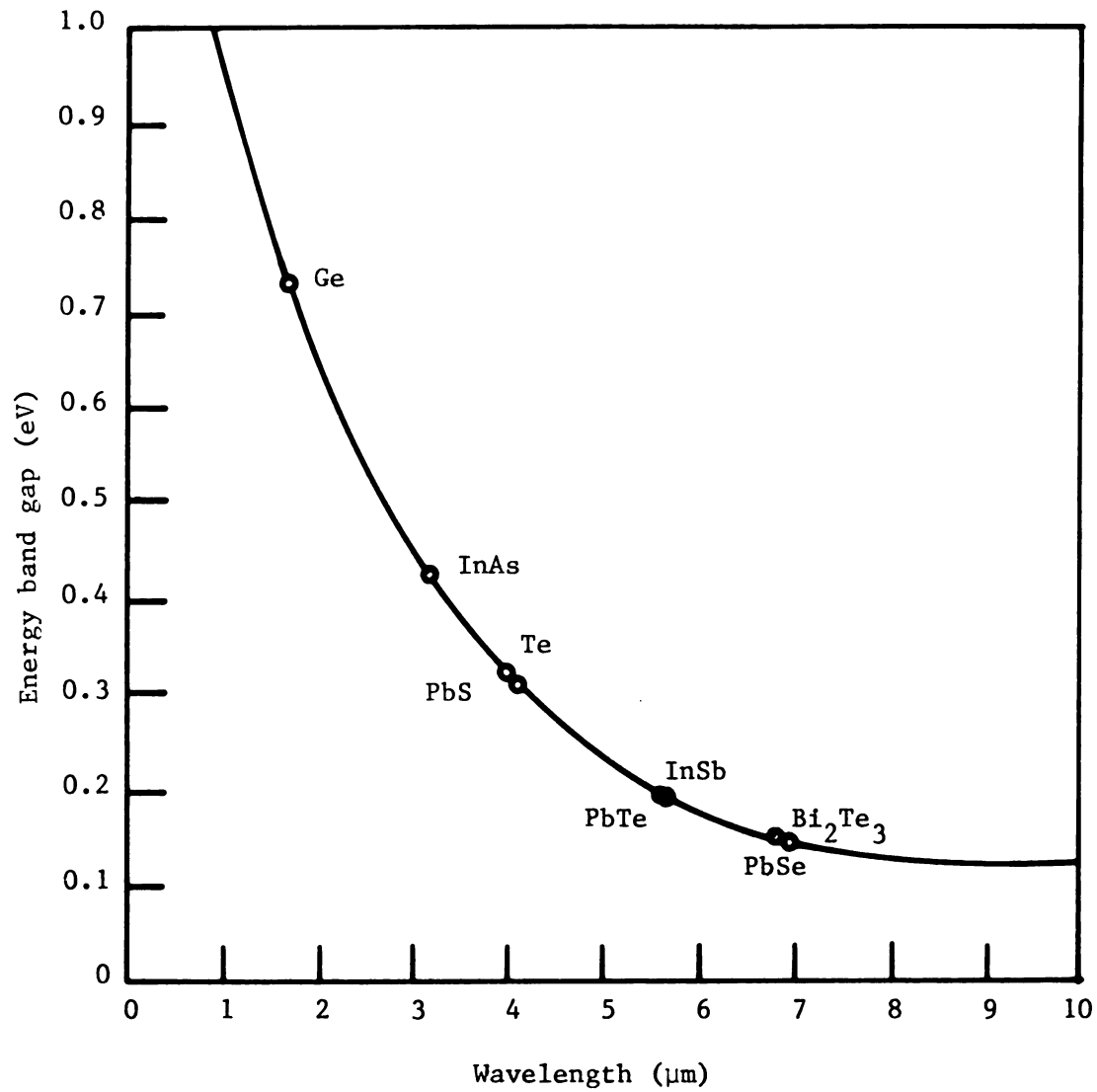


Figure 1. Energy band gap versus maximum detector wavelength. Included points represent a number of common materials. (From Stevens, Ref. 3)

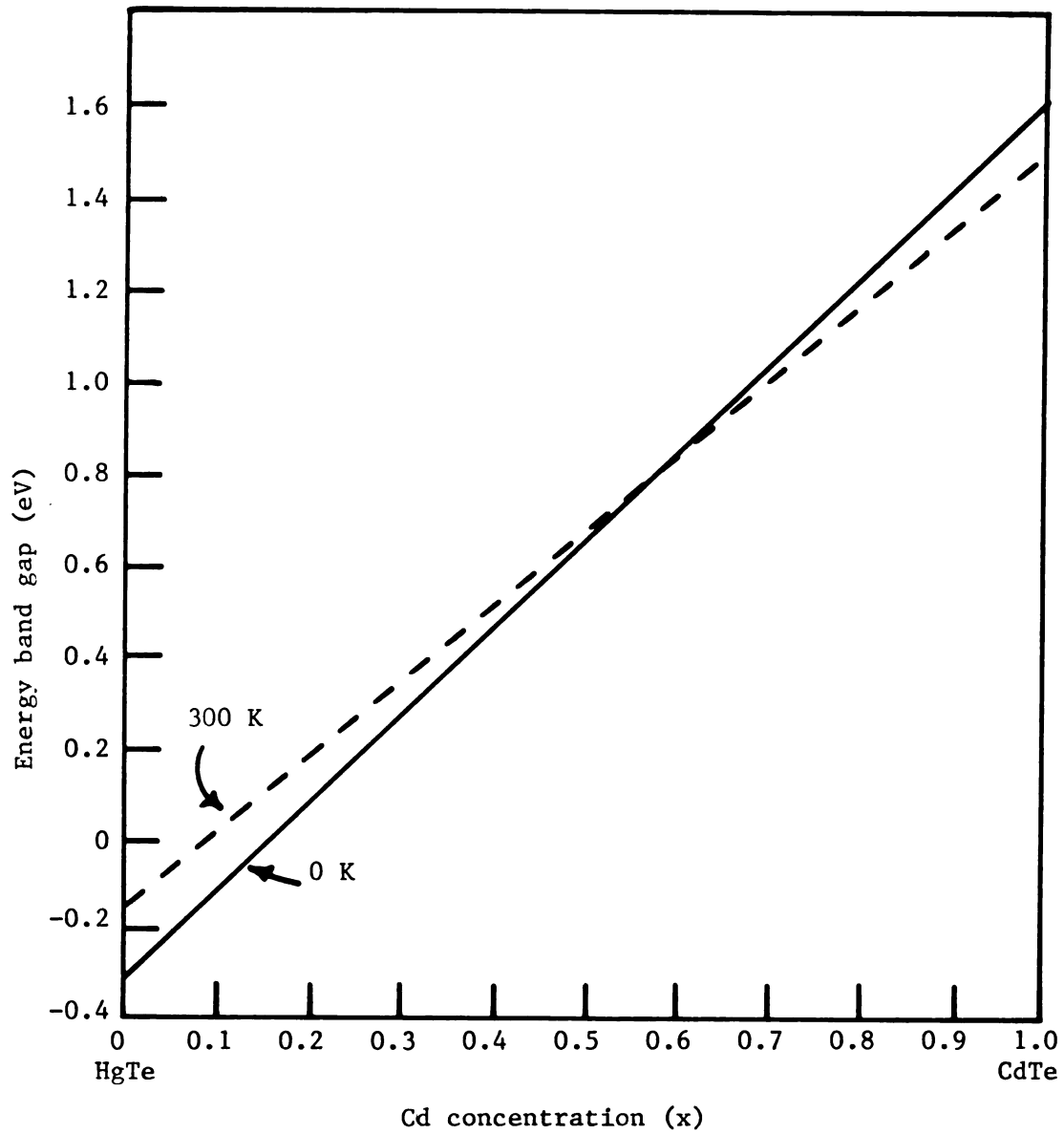


Figure 2. $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ Energy band gap as a function of Cd concentration (From Kruse, Ref. 6)

much debate concerning what substrate produces the best epilayer. At the present time CdTe is one of the most widely used because of the rather small (0.3% for $x = 0.2$) lattice mismatch between the (111) crystal orientation of CdTe and $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$. Also, CdTe substrates can be grown in single crystal form and are transparent to infrared radiation ($E_g = 1.6 \text{ eV}$) which is important for some device geometries.

CdTe Crystal Growth⁷

CdTe single crystals are grown by the Bridgman method. Equal atomic amounts of Cd and Te are loaded into a sealed ampoule which is lowered through a vertical furnace. A temperature gradient is set-up to ensure directional crystalization of the CdTe at the bottom of the ampoule. The upper portion of the growth chamber is held at the higher temperature to prevent sublimation and vapor growth at the top of the ampoule. The growth shape of the liquid-solid interface is determined by the temperature isotherms in the ampoule.

$\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ Epilayer Growth

$\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ epilayers are most often grown on (111) oriented single crystal CdTe substrates by liquid phase epitaxy (LPE). Other epitaxial growth processes such as molecular beam epitaxy (MBE), vapor phase epitaxy (VPE), and organometallic vapor phase epitaxy

(OMVPE) are in the experimental stages but at present are too expensive to be used for large scale production.⁸ An epilayer is defined as a smooth, continuous single crystal film grown on a substrate such that the film crystal structure corresponds to and is determined by that of the surface of the single crystal substrate.⁴ A melt of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ is formed just above the liquidus temperature at one end of a closed quartz ampoule. At the other end a CdTe substrate is mounted and externally cooled. Once the ampoule reaches thermal equilibrium, it is inverted to allow the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ melt to flow onto the substrate and crystalize. After the epilayer is obtained, the ampoule is inverted back to its original position to decant the remaining $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$.⁹

Epilayer-Substrate Interaction

During LPE growth, there is substantial interaction at the epilayer-substrate interface. Not only is there a mixing of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ and CdTe (see Figure 3) but also any defects or impurities in the first 10 to 20 μm of the substrate should be expected to affect the epilayer. It is these defects or impurities in the substrate that are believed to degrade infrared detector devices and hence provide the motivation for this project. Defects or impurities which propagate into the epilayer appear as electronic levels in the energy band gap causing excessive noise and shorter carrier lifetimes in a device.¹⁰

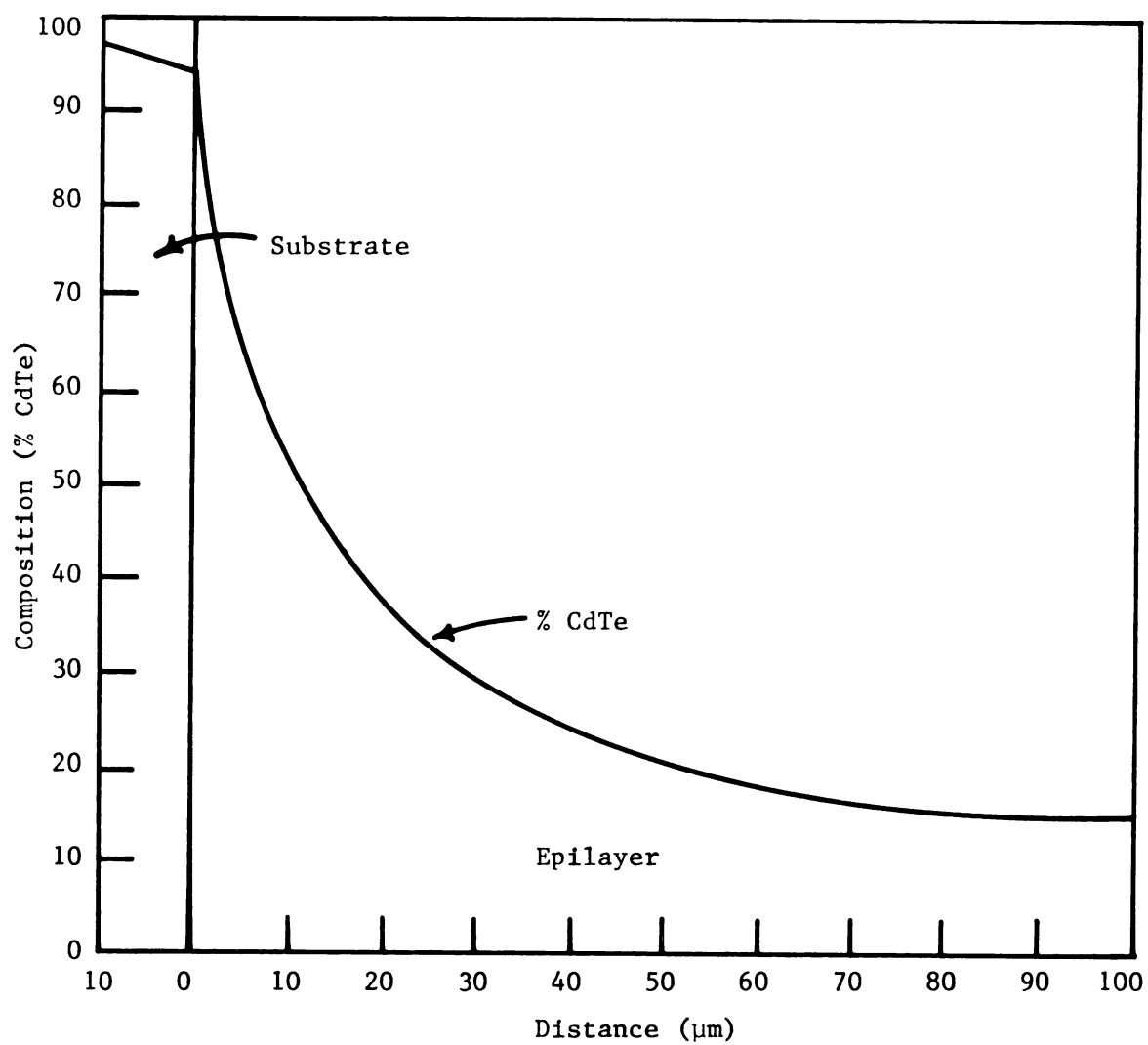


Figure 3. Composition profile of epitaxial $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ on CdTe substrate as a function of depth.
(From Micklethwaite, Ref. 9)

These electronic levels in the energy band gap were studied by groups at Grenoble, Rockwell International, California Institute of Technology, Honeywell, Westinghouse, and Hughes Aircraft using both optical and electronic techniques. Molva et. al.^{11,12,13} characterized impurities (especially Cu and Ag) in CdTe using low temperature (4K) photoluminescence studies of exciton recombinations. Bajaj et. al.¹⁴, using the same techniques at 77K have characterized CdTe substrates which are both "good" and "bad" (in terms of the quality of LPE $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ grown on them) by studying the broad donor-acceptor transitions. S.H. Shin et. al.¹⁵ saw Te deposits in CdTe substrates using Auger Spectroscopy. Such deposits are detrimental to CdTe crystallinity which affects $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ epilayer quality. Hunter et. al.¹⁶ also used photoluminescence of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ to show how surface concentration gradients can be mapped. Polla et. al.^{17,18} studied deep level transient spectroscopy of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ to characterize defect energy levels relative to the band gap.

Scanning electron microscopy of defects at the epilayer-substrate interface have been studied by James et. al.¹⁹ Also, Wood et. al.²⁰ used transmission electron microscopy to characterize epilayer-substrate interfaces for both defects and chemistry. Wood used x-ray fluorescence spectroscopy to study Hg concentrations in the interface region of a $\text{Hg}_{0.9}\text{Cd}_{0.2}\text{Te}$ epilayer on CdTe.

Despite all the work that has been done related to epitaxial detector devices, to date it is not clearly understood exactly how a

substrate interacts with an epilayer to degrade a device. More experimental work is needed to investigate the chemistry of substrates and the defect propagation at the epilayer-substrate interface.

CdTe Substrate Studies at Michigan State University

Because very little is known about the micro-chemistry of CdTe substrates used for epilayer growth, we performed x-ray fluorescence spectroscopy in conjunction with electron microscopy. The x-ray fluorescence spectroscopy available in a scanning transmission electron microscope is a powerful analytic tool for studying micro-chemical inhomogeneities on a scale of several hundred angstroms for impurity concentrations as small as 0.05 atomic percent.

Special sample preparation is necessary for our electron microscopy studies and has been developed in collaboration with Eun-Hee Cirlin at the Rockwell International Science Center. A sample preparation technique has been developed to produce self-supporting 3mm discs of CdTe having a microscopic perforation with edges 1000Å or less in thickness.

Rockwell International has provided a random selection of CdTe substrates - three Rockwell grown samples CdTe 3-268, CdTe 2-36, and CdTe 4-2; and three II-VI Inc. grown samples CdTe 1949 (a "good" substrate), CdTe 3531 (a "bad" substrate), and CdTe: Cu 2303 (doped

in the melt with $\sim 10^{16}$ Cu). We prepared and studied these samples for stoichiometry and impurities.

II. X-RAY FLUORESCENCE SPECTROSCOPY

Electron Microscopy

In an electron microscope, when beam electrons interact with an electron transparent sample, information concerning chemistry, crystallinity, thickness, and topology is generated. The processing of this information can be accomplished by properly positioning the appropriate detector system along the beam axis as shown in Figure 4. Signal generation and processing will be discussed for x-ray fluorescence spectroscopy as generated in a VG HB501 Scanning Transmission Electron Microscope (see Figure 5). This microscope is equipped with a high resolution, field emission electron gun to provide a 100 KeV electron beam. A double condenser lens system is used for increased probe forming flexibility along with a single, high excitation objective lens. The microscope is also equipped with a cold stage which cools the sample area to -136°C and a tilt stage with orthogonal angle ranges of $\theta_x = \pm 60^{\circ}$ and $\theta_y = \pm 60^{\circ}$. The x-ray micro-analysis system is a LinkS Si(Li) detector interfaced to a Tracor-Northern 2000 computer. These basic features of the microscope are illustrated in Figures 6 and 7.

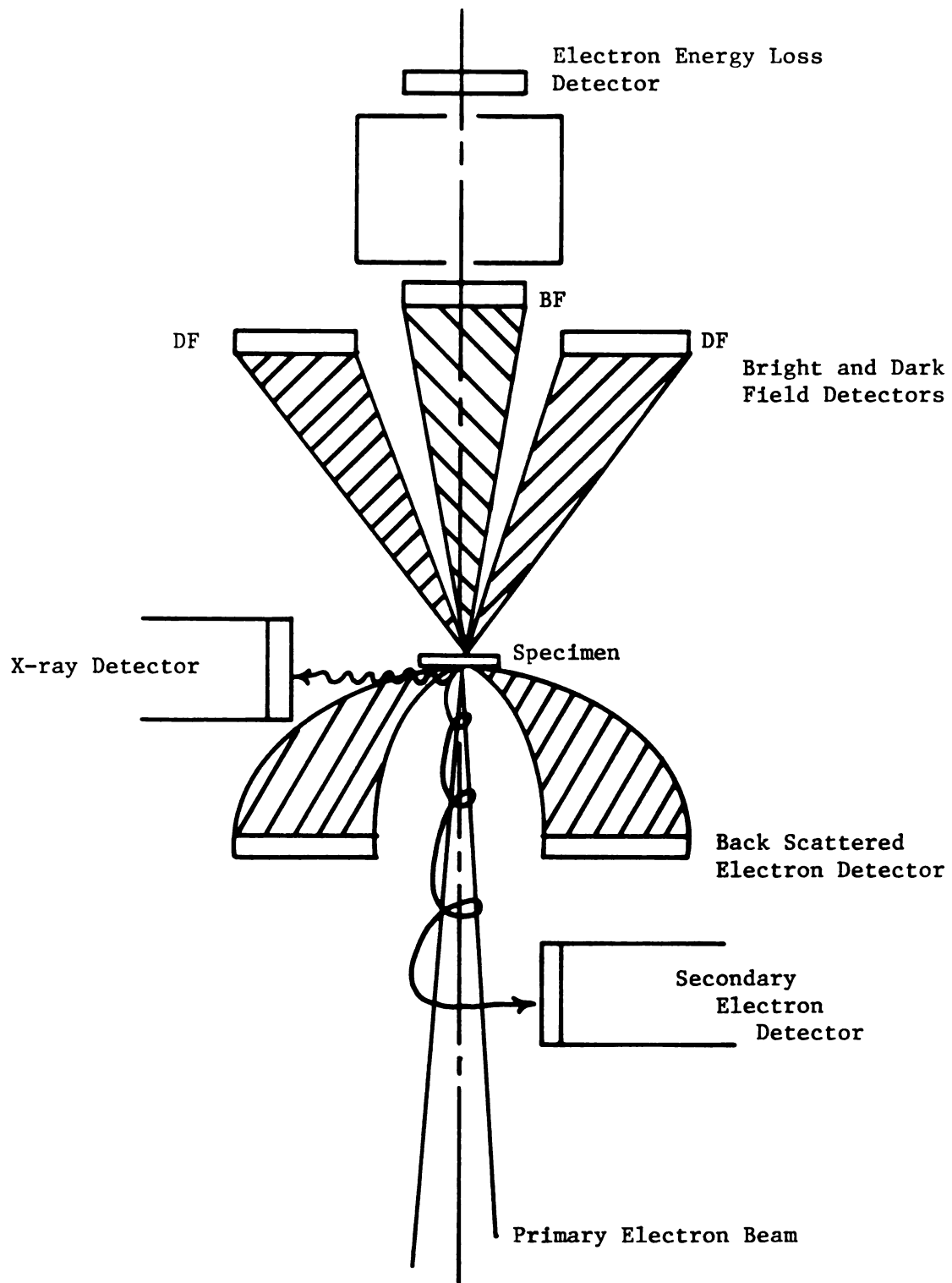


Figure 4. Schematic view of various signal detectors used in analytical electron microscopy.



Figure 5. Console and column of the VG HB501
Scanning Transmission Electron Microscope.

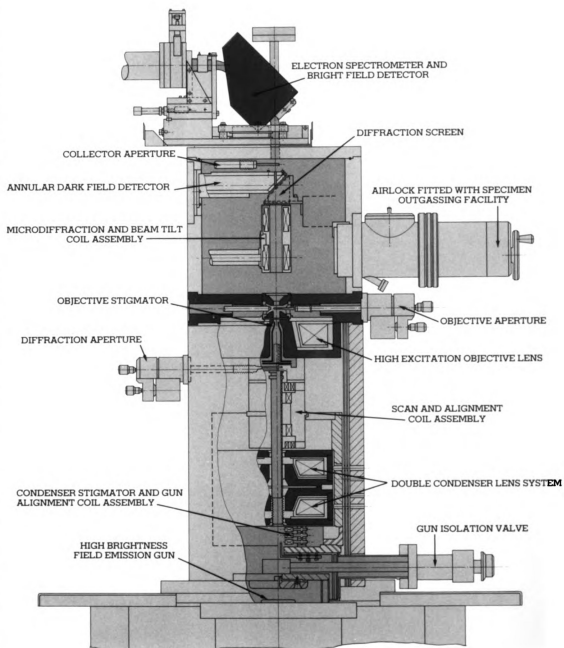


Figure 6. Schematic view of VG HB501
Scanning Transmission Electron Microscope column.

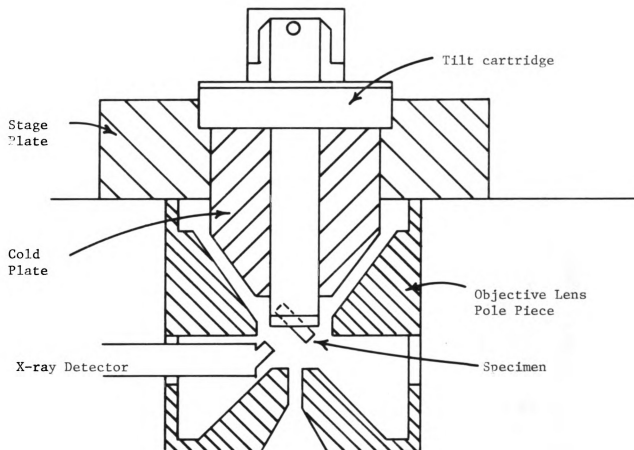


Figure 7. Sample area cross- section of VG HB501 Scanning Transmission Electron Microscope.

X-ray Production and Detection

In an electron microscope, beam electrons interact with atomic electrons via energy transfer. An atomic electron gains energy and is excited out of its ground state leaving a vacancy. This vacancy is filled by a higher energy level atomic electron which fluoresces in the x-ray energy range in order to shed its excess energy. X-rays produced from L shell, M shell, or N shell atomic electrons which fill a vacancy in the K shell are referred to as K_{α} , K_{β} and K_{γ} x-rays respectively. In addition, x-rays produced from M shell or N shell atomic and electrons which fill a vacancy in the L shell are referred to as L_{α} and L_{β} x-rays respectively. Figure 8 illustrates the excitations involved in x-ray production. The K_{α} and L_{α} x-rays typically have the highest production cross sections due to the nature of dipole interactions.

Each atom has a different set of energy levels, hence a unique x-ray fluorescence spectrum. It is this uniqueness that makes x-ray fluorescence spectroscopy a powerful tool for chemical analysis.

The x-rays generated by the beam-sample interaction are detected by a 30mm² cross-sectional area Si(Li) detector system which consists of an 8 μ m Be window, 200Å gold layer, 1000Å Si dead layer, and a 3mm Si active region as shown in Figure 9. The x-ray detector is liquid nitrogen cooled and mounted at a 13° angle off the zero tilt plane of the sample. During x-ray data acquisition, the sample is tilted toward the detector at the tilt setting of

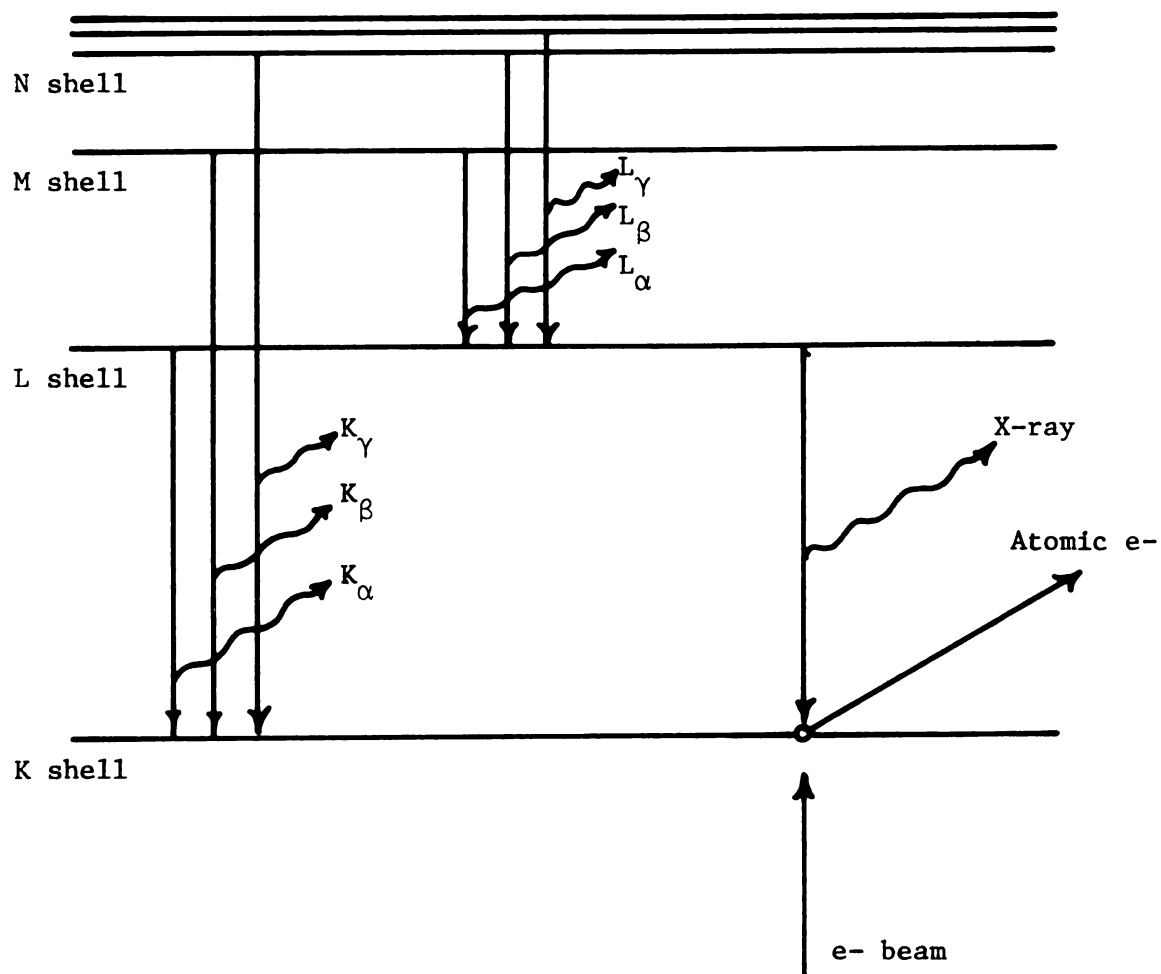


Figure 8. Energy level scheme illustrating x-ray production.

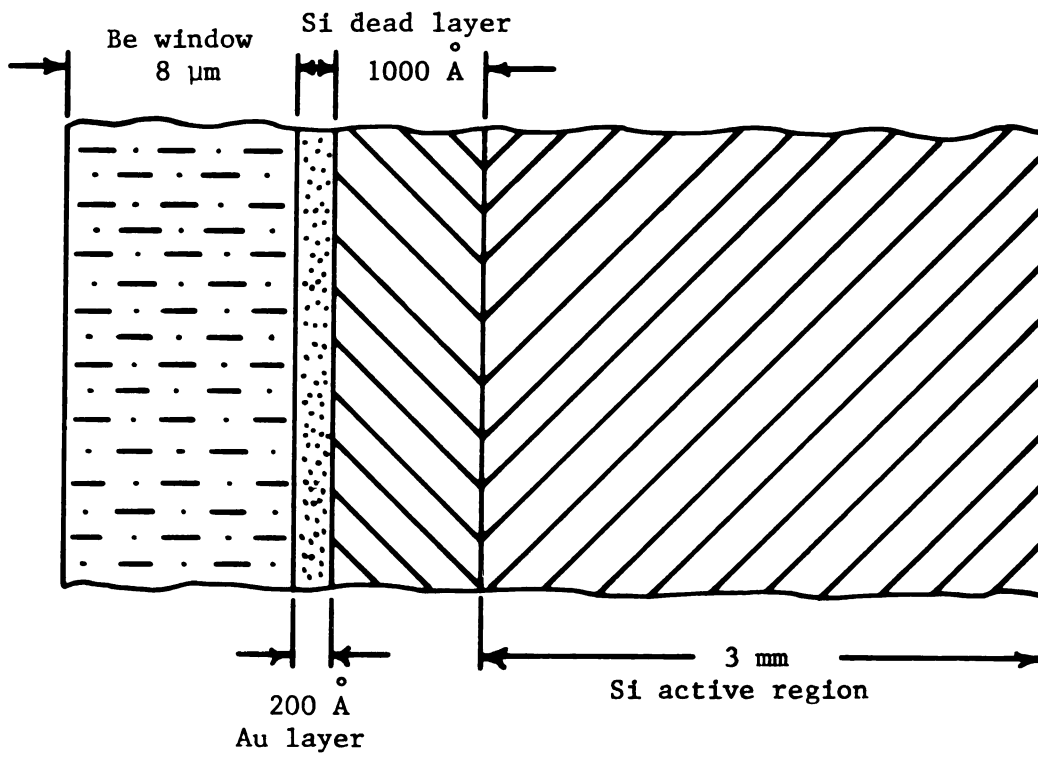


Figure 9. Cross-section view of Links detector system.
(not to scale)

$\theta_x = -20^\circ$ and $\theta_y = 20^\circ$. These tilt angles provide the highest (L_α/K_α) peak ratios for both Cd and Te x-ray lines as shown in figures 10 and 11. This insures that the system absorption is minimized and that the sample-detector geometry is maximized.

X-ray Data Corrections

When a 20 Å diameter electron beam impinges on a sample, the beam spreads rapidly in the fashion indicated in Figure 12. The sample volume in which the x-rays are produced depends strongly on the sample thickness.

The integrated count rate of characteristic K_α or L_α x-rays from element A (or B) which have been detected is a complicated function of sample parameters, detector efficiency, and beam-sample-detector geometries. For thin film samples of thickness dt this function can be linearized to the expression shown in equation 2.²¹

$$I_A dt = \delta_A k_A \epsilon_A n C_A dt \quad (2)$$

where

- $I_A \rightarrow K_\alpha$ or L_α integrated count rate of element A
- $\delta_A \rightarrow$ absorption correction of element A in the sample
- $k_A \rightarrow$ fluorescence parameter (k-factor) for x-ray line of element A
- $\epsilon_A \rightarrow$ detector efficiency for x-ray line of element A
- $n \rightarrow$ number of electrons bombarding dt
- $C_A \rightarrow$ weight percent concentration of element A

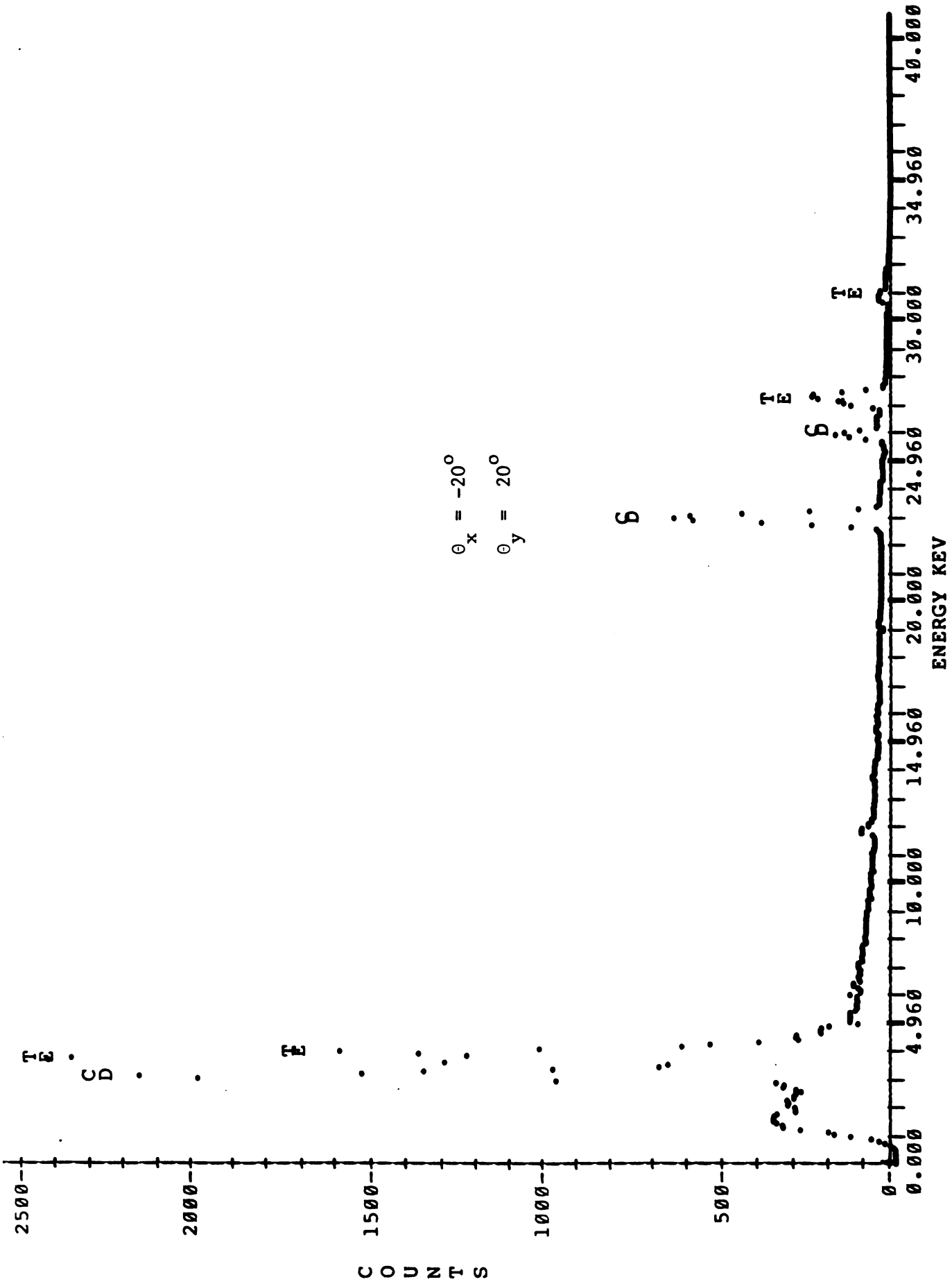


Figure 11. CdTe x-ray spectrum at optimum tilt angles.

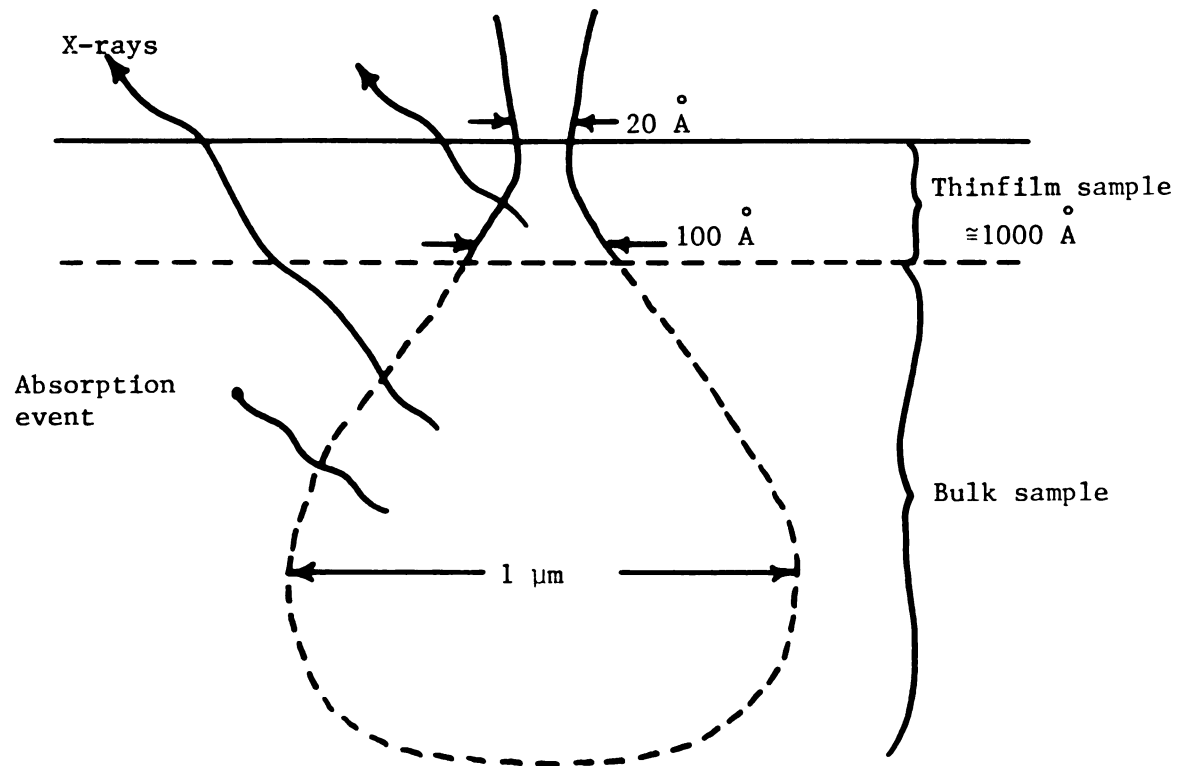


Figure 12. X-ray production for thin film and bulk samples. (From Williams and Edington, Ref. 22)

In using equation 2 to calibrate the integrated count rate of an x-ray line from an element of unknown weight percent concentration, a "standard" x-ray line from a known weight percent concentration must be included in the sample and appear in each spectrum. This is not a trivial task. However, a standardless technique can be used to determine a weight percent concentration ratio between two elements in the same sample.²¹ The equation for this standardless technique is

$$\frac{I_A}{I_B} = \frac{\delta_A k_A \epsilon_A C_A}{\delta_B k_B \epsilon_B C_B} \quad (3)$$

Furthermore, for thin film samples (thickness $\sim 1000\text{\AA}$) it will be shown that absorption corrections associated with the standardless technique (δ_A/δ_B) are at most a few percent and can be neglected. Thus for standardless, thin film samples the weight percent concentration ratio for two elements is

$$\frac{C_A}{C_B} = \frac{k_B \epsilon_B I_A}{k_A \epsilon_A I_B} \quad (4)$$

All weight percent concentration ratios will be done using K_α x-ray lines because of their superior resolution in comparison with the L_α x-ray lines. This resolution is important for the Cd (A=48) and Te (A=52) lines as shown in Figure 13. The information necessary for k-factor and detector efficiency calculations of Cd, Te and the impurities found in the CdTe samples has been published by Zaluzec²³ and is listed in Table 1.

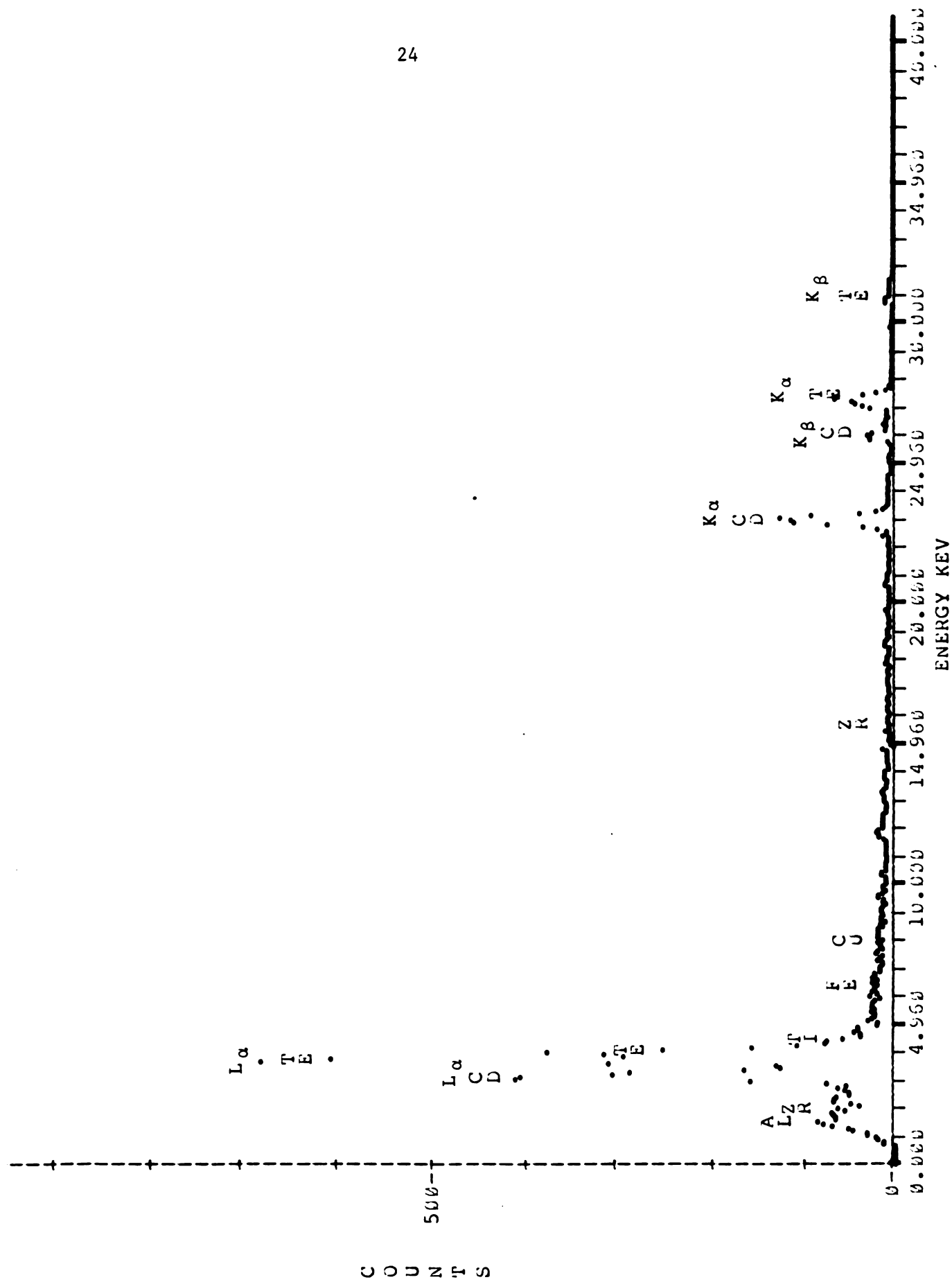


Figure 13. CdTe: Cu 2303 x-ray spectrum enumerating x-ray lines for Cd and Te.

Table 1. Raw data correction factors for K_{α} x-ray lines

Element	k_A -factor	ϵ_A	$\frac{k_{Cd} \epsilon_{Cd}}{k_A \epsilon_A}$
Cd	0.3685	0.84356	---
Te	0.2697	0.67661	1.7
Fe	2.0890	0.98032	0.15
Cu	1.7493	0.98933	0.18
Zr	0.6717	0.99087	0.47
Al	4.4280	0.70418	0.10
Ti	2.4734	0.95053	0.13

Let us now consider absorption effects. When an atomic electron fluoresces, the generated x-ray can be absorbed by another atomic electron elsewhere in the sample, hence decreasing the measured intensity. This effect is dependent on the beam-sample-detector geometry, sample topology, and sample thickness (see Figure 14). The microscopic sample topology is not known exactly. The best that can be done is to assume that a uniform wedge shaped edge results from the jet thinning process. It is also not possible to determine the exact thickness of an edge. However, if an edge is thin enough to give a good bright field image, the thickness is on the order of $1000 \text{ \AA}$ or less. Absorption calculations for the standardless technique determined for Cd and Te K_{α} lines, with the additional assumption that $C_{\text{Cd}} + C_{\text{Te}} = 1$, show corrections of approximately 1% for a CdTe sample thickness of $10 \text{ }\mu\text{m}$. Hence absorption terms for Cd and Te in standardless, thin film CdTe samples are negligible and equation 4 can indeed be employed.

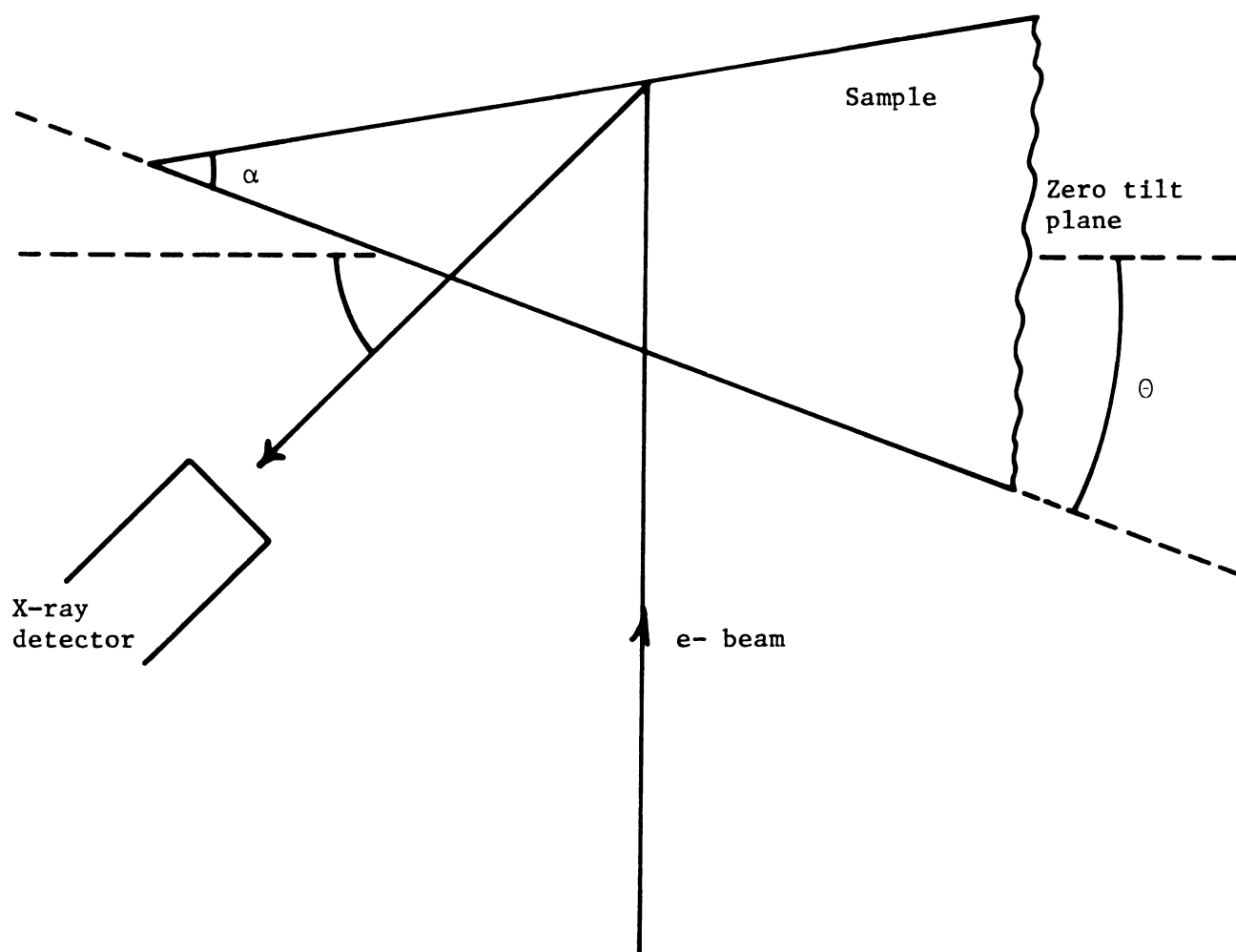


Figure 14. Beam- sample- detector geometry.

III. SAMPLE PREPARATION

Introduction

In electron microscopy, sample preparation is by no means a trivial procedure. The desired end result is a region of the sample less than $1000\text{\AA}$ in thickness which is physically and chemically equivalent to the bulk material from which the sample was prepared. For this reason, it is important to develop special handling and etching techniques which do not contaminate or alter the microscopic characteristics of the sample in the region which is to be studied.

Typically semiconductor, single crystal materials are soft, yet brittle, in comparison with metals; thus, classical polishing techniques tend to create and propagate defects. This needs to be avoided. Also, when dealing with binary and ternary compounds, preferential etching must be guarded against. For these reasons, static and semistatic chemical etching techniques have been developed for use with semiconductor materials. For CdTe and $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ it has been determined that bromine in methanol (MeOH) or hydrobromic acid (HBr) are the most effective chemical etchants. The bromine bonds with the cation to form a cation-Br salt which is carried away along with the Te by the methanol (or hydrobromic acid). The concentration for the maximum etching rate is about 4% Br in methanol (or hydrobromic acid). Any higher concentration of

bromine appears to form the salt faster than it can be carried away; hence, slowing the etching process and leaving an unwanted bromine contamination layer as shown in the x-ray spectrum in Figure 15.

Keeping in mind that CdTe is used as a substrate for LPE growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, the important region of the CdTe substrate is the surface on which the epitaxy is grown - the "top surface" of our samples. We wish to analyze this top surface for any chemical or structural differences which may exist between various CdTe samples.

It is crucial to manipulate the top surface of the CdTe sample as little as possible during sample preparation. For this reason, the area that will eventually be thinned to less than $1000\text{\AA}$ must not be touched by hands or metal objects. Plastic gloves and plastic tweezers should always be used until a thinned region has been clearly defined, then vacuum tweezers can be used.

An electron microscope, self-supporting sample must be 3mm in diameter and about $150\text{ }\mu\text{m}$ thick. The center portion of the disc must have a perforation with edges which are no more than $1000\text{\AA}$ thick (see Figure 16).

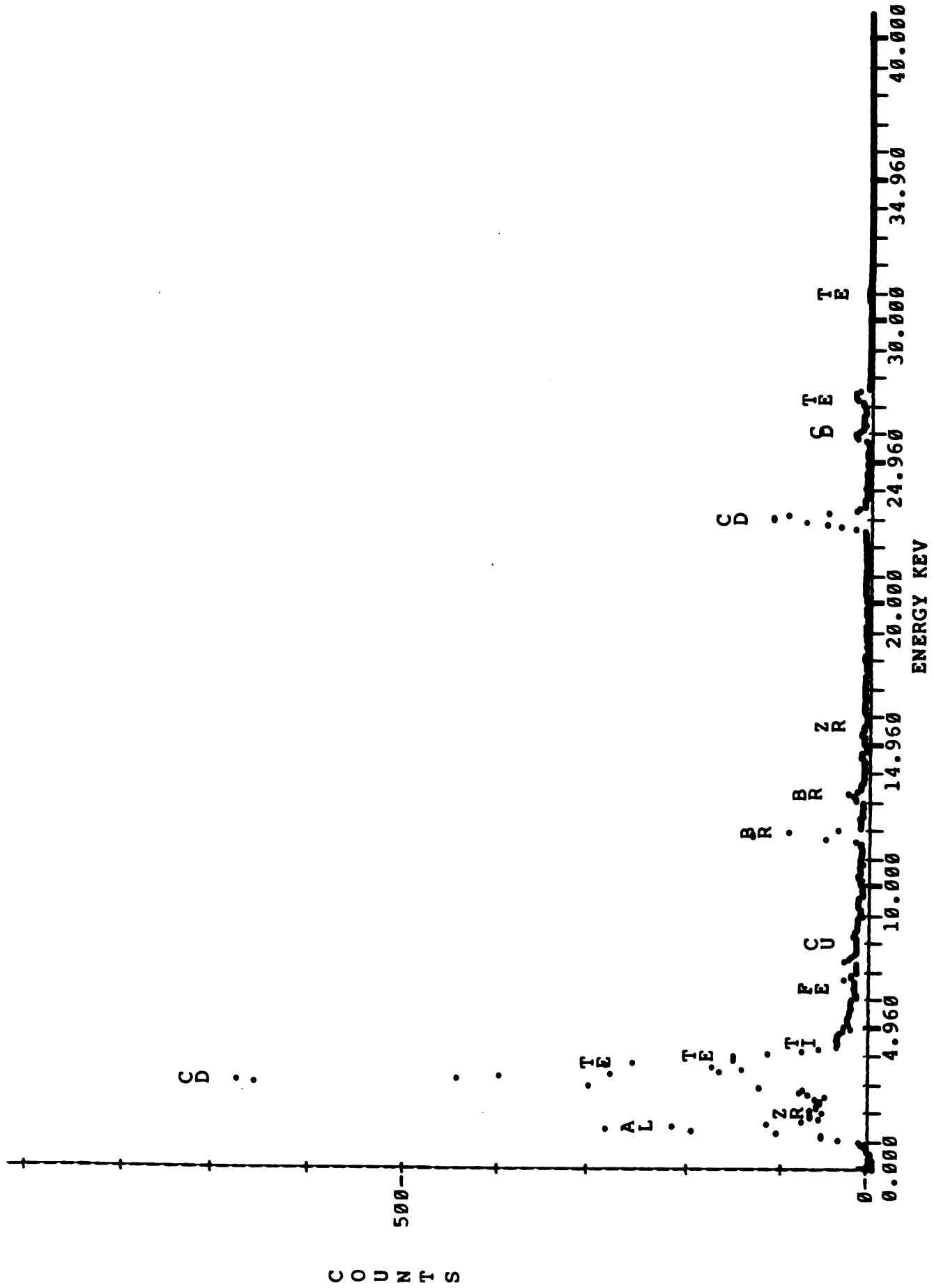
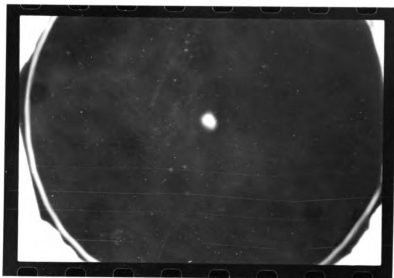


Figure 15. CdTe 2-36 x-ray spectrum showing Br contamination.



1 mm |—————|

Figure 16. Top surface of CdTe disc with center perforation.

CdTe Top-Surface Preparation and Etching

Starting with a 600 μm thick bulk piece of CdTe, an initial etch is performed to remove $\sim 25\text{ }\mu\text{m}$ from the top surface. This step is also done prior to LPE growth as it removes any mechanical surface damage, leaving a clean CdTe surface. A photoresist masking technique is then used to obtain the proper disc geometry. Shipley 1375 photoresist has been chosen because it has good adhesive properties and is insoluble in both HBr and water. 1375 photoresist is a light sensitive, viscous liquid which undergoes a positive photographic process when exposed to ultraviolet light. A uniform thin layer, which is necessary for good results, can be applied with an eyedropper while spinning the CdTe sample at 3000 rpm. We have designed a simple spinner system which utilizes a scotch tape sample mounting technique (see Figure 17). The photoresist mask itself is a thin piece of clear plastic on which is mounted an array of 3mm discs which are opaque to ultraviolet light. Note that the array side of the mask is referred to as the top side.

Once exposed and developed, a well shaped 3mm photoresist disc will be left on the top surface of the CdTe sample to protect a circular region from the etchant. A Br/HBr solution is used to etch a 150 μm plateau into the CdTe as shown in Figure 18. This plateau becomes the desired disc after the back side is etched away.

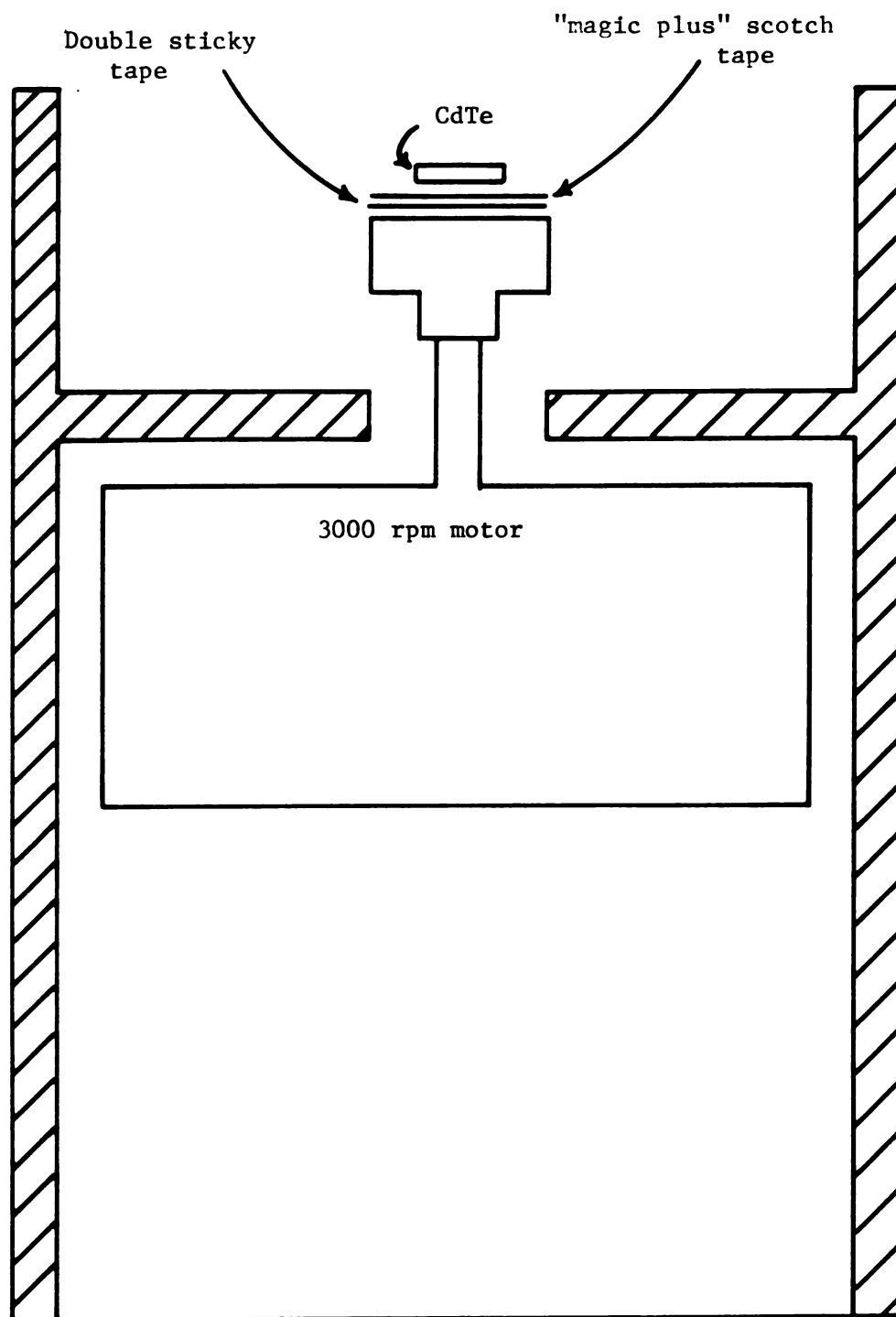


Figure 17. Spinner for photoresist application.

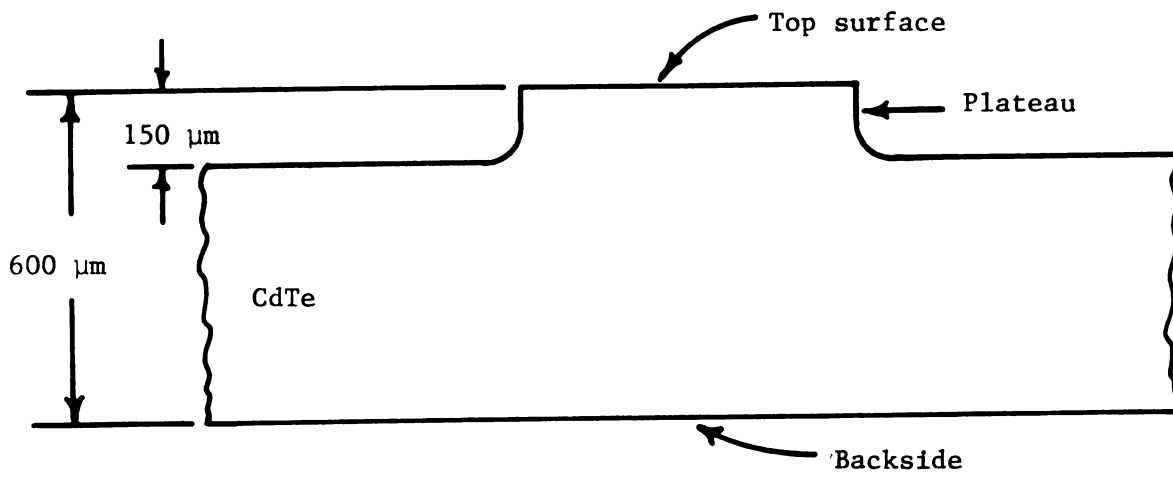


Figure 18. CdTe after top surface etching.

CdTe BackSide Preparation and Etching

We have developed a semistatic procedure for back side etching. The etching process of Br in methonal (or hydrobromic acid) exhibits a "melting" characteristic which attacks sides and edges as well as surfaces. The more the back surface is etched away, the faster the sides etch inward. This action tends to destroy the disc before it can be retrieved. To counteract this tendency, a thin bead of photoresist is painted on the sides and back edge in addition to the protective layer applied to the CdTe top surface. This forces the etching action to cut its own edges allowing the entire unprotected back side to "melt" uniformly to the point where the disc appears intact. Due to the large amount of CdTe which must be etched away, the stirring action of a small magnetic "peanut" and stirring plate are employed to continually refresh the etchant in contact with the sample. Exceptionally good results have been obtained with this method, however it typically takes 6 to 9 hours to remove the back side.

Jet Thinning

The last step in sample preparation is to jet thin from the back side of the CdTe disc such that a microscopic perforation is produced on the top surface. The edge of this perforation is thin enough to be analyzed in the electron microscope. We have employed a South Bay model 550C jet thinner modified for chemical etching. It has an automatic LED sensor system which can be set to stop the

jet action at the point when the microscopic perforation is made in the CdTe disc. The sample is mounted in the holder with Apiezon M grease in such a way that only the center 1mm area is exposed to the etchant. This allows a well shaped dimple to form. Also, the grease protects the covered CdTe area from the etching solution. The adhesive properties of the grease are adequate to hold the CdTe disc firmly in place against the jet action. Apiezon M is also insoluble in Br/methonal but readily soluble in toluene.

A step-by-step procedure of the above sample preparation can be found in Appendix A.

IV. RESULTS

Data Acquisition

CdTe substrates were analyzed for stoichiometry and impurities using both quantitative and qualitative x-ray fluorescence spectroscopy. For quantitative analysis, spot acquisitions (using a 20 μ m beam diameter) of 100 seconds per spectrum were studied. Integrated K_{α} peak intensities are typically on the order of several hundred counts. An example of a spot acquired x-ray fluorescence spectrum is shown in Figure 19. Qualitative analysis was performed using x-ray fluorescence mapping techniques. The scanned sample area under study was assigned a 128 x 128 pixel matrix. A region of interest (ROI) was defined at the x-ray energy of the K_{α} line for each elemental map as shown in Figure 20. As the beam scans the sample area, data is acquired at each spot for 0.07 seconds and is stored in a bin corresponding to the appropriate pixel. Two main points of information are obtained using x-ray mapping. First, any gross impurity is clearly identifiable and second, an increase in thickness is observed as an increase in intensity. For each sample mapping area the intensity scale limits are defined on the Cd map. A linear relationship between pixel counts and a color scale is assigned where the minimum counts in a pixel corresponds to black and the maximum counts in a pixel corresponds to white on the x-ray map. An example of a x-ray fluorescence map is shown in Figure 21.

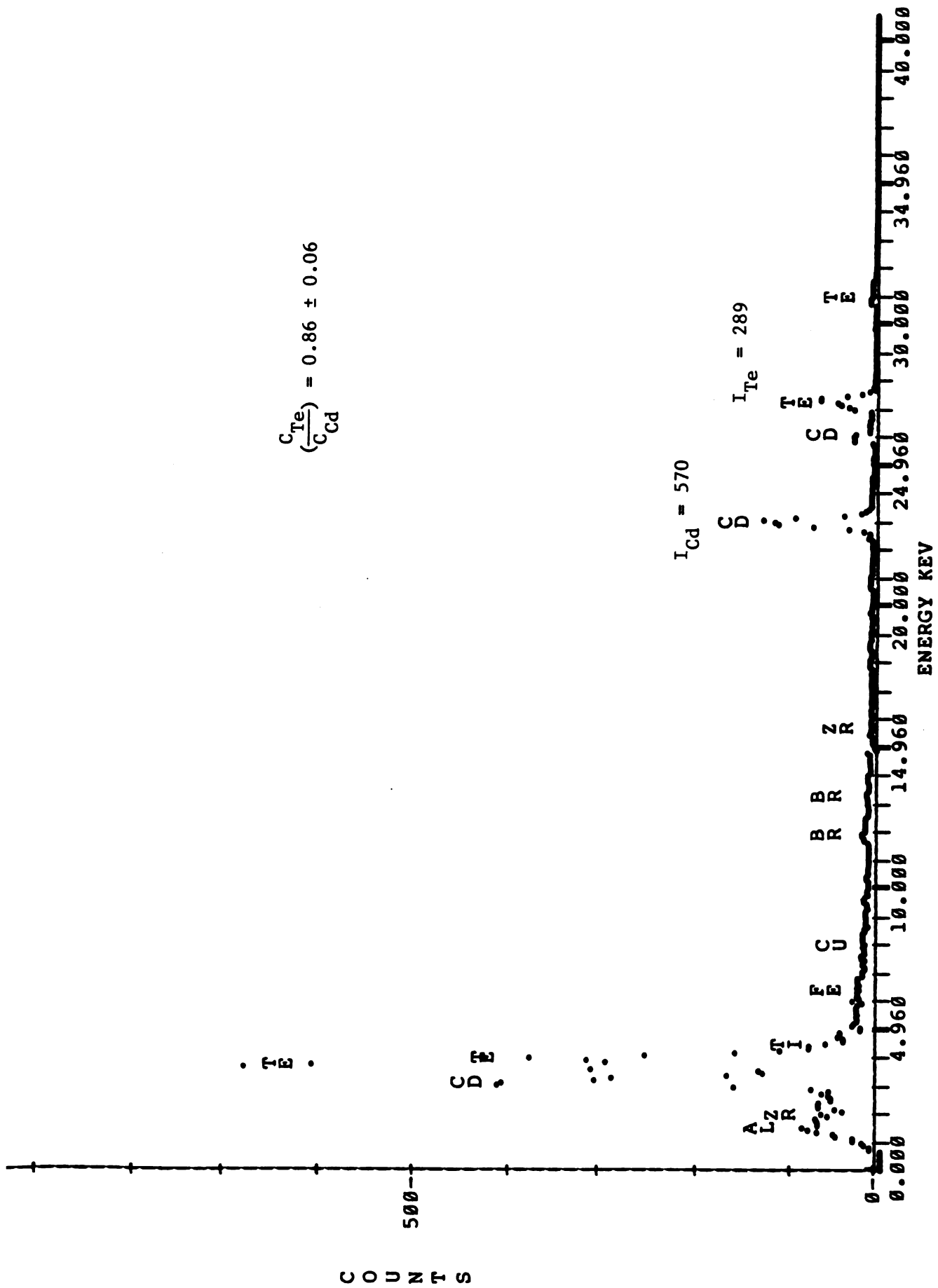


Figure 19. CdTe: Cu 2303 x-ray production showing K_{α} peak integrated counts.

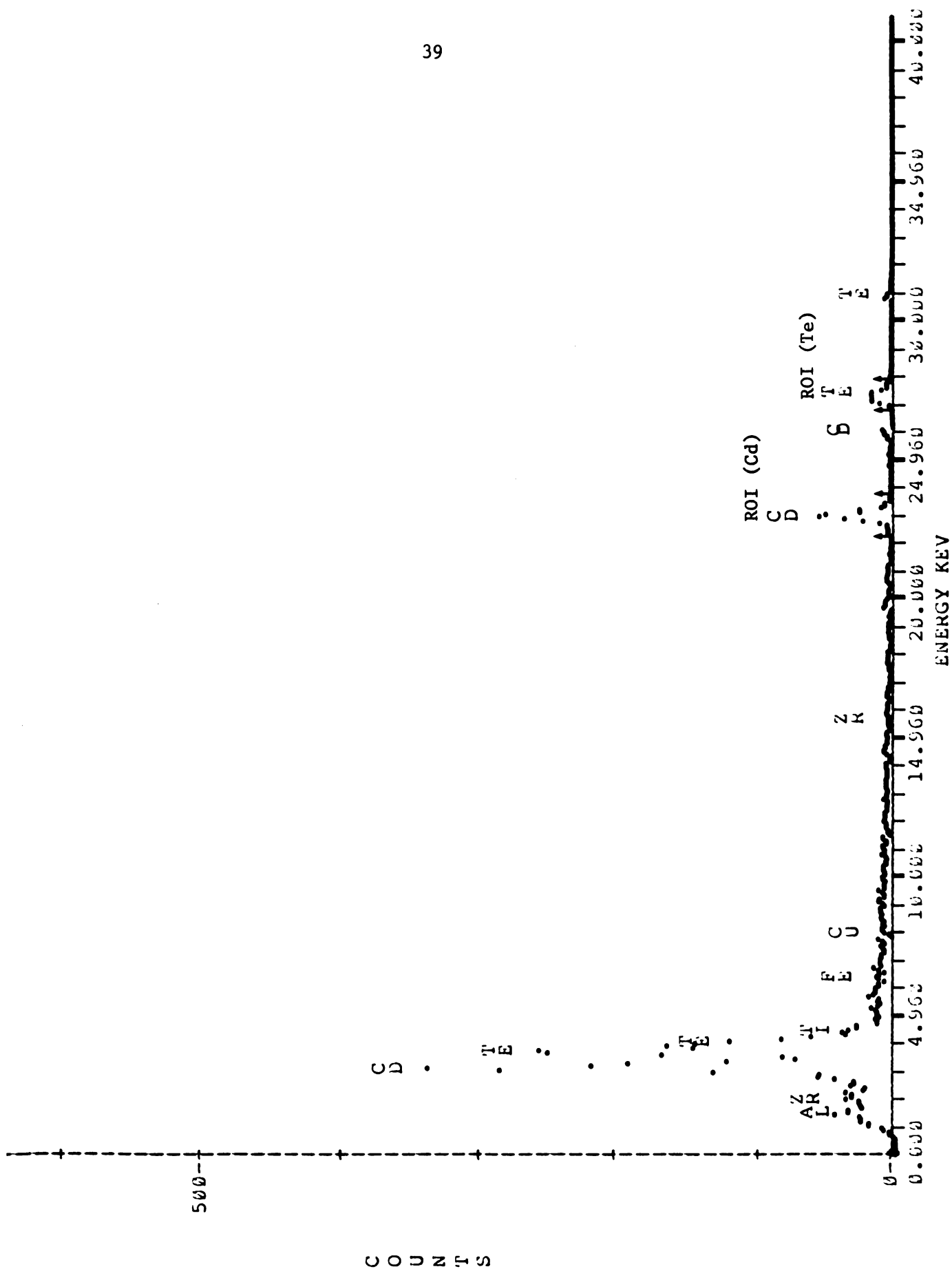


Figure 20. CdTe 2-36 x-ray spectrum showing region of interest (ROI) definition.

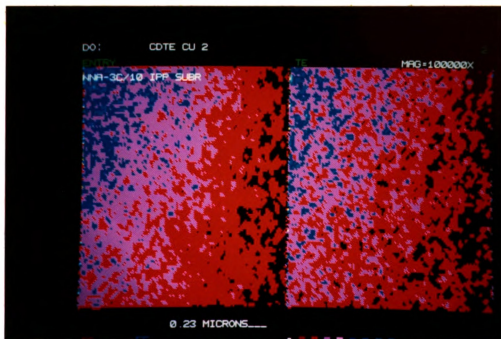
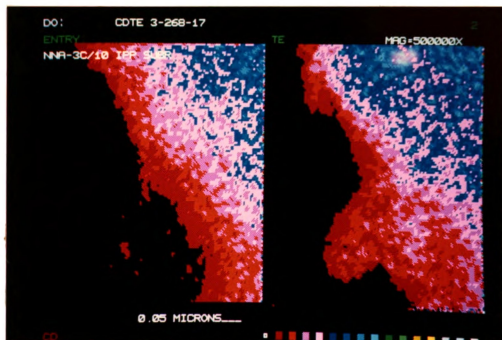


Figure 21. Example of an x-ray map for CdTe: Cu 2303
(Cd map on the left and Te map on the right).

The six CdTe samples that have been analyzed are discussed below.

CdTe 3-268

Areas that are high in Te and low in Cd were seen in CdTe 3-268. These Te deposits were oval in shape and on the order of $1000\text{\AA}$ along the long axis. They were typically found in clusters of 2-5 deposits which seemed to be randomly distributed throughout the sample. Examples of the Te deposits are shown in Figures 22 and 24 with spot acquired spectra for these regions shown in Figures 23 and 25 respectively. Figure 26 illustrates a spot acquired x-ray fluorescence spectrum obtained in a region away from Te deposits. The average weight percent concentration ratio of Te to Cd determined from four such spectra for CdTe 3-268 was found to be 0.95 ± 0.05 .



See Figure 23



Figure 22. X-ray map of Te deposits in CdTe 3-268
(Cd map on the left and Te map on the right).

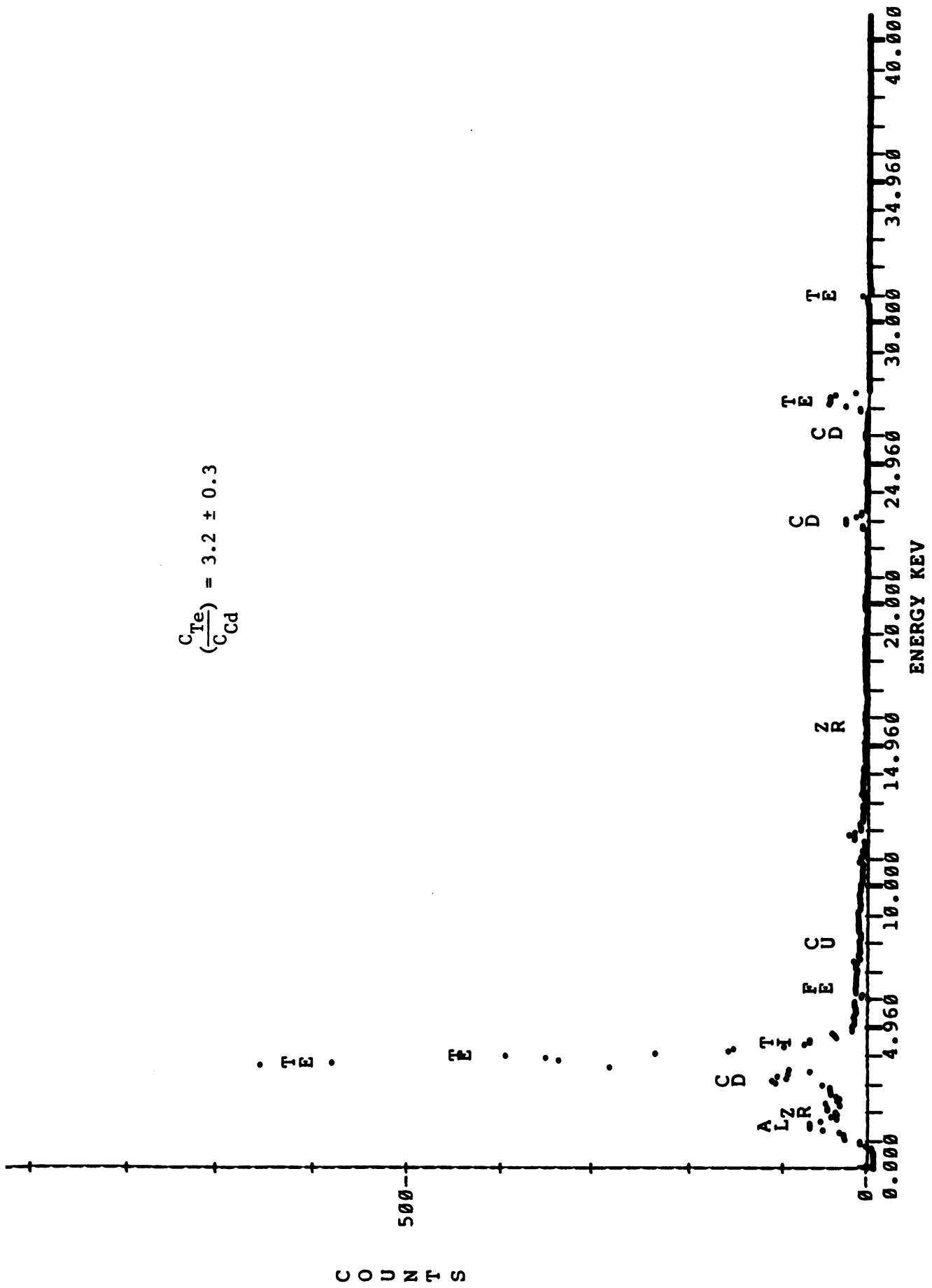
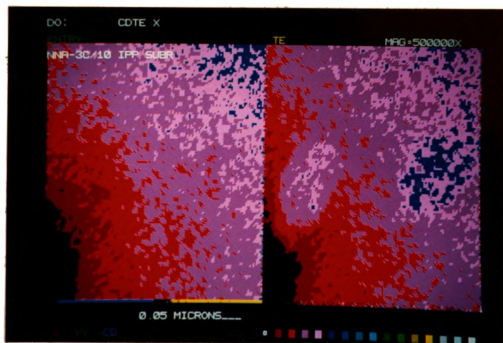


Figure 23. CdTe 3-268 x-ray spectrum of Te deposit shown in Figure 22.



See Figure 25

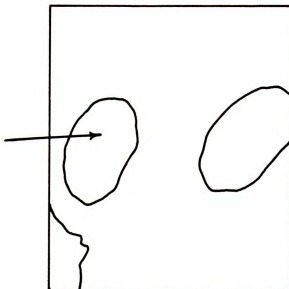


Figure 24. X-ray map of Te deposit in CdTe 3-268
(Cd map on the left and Te map on the right).

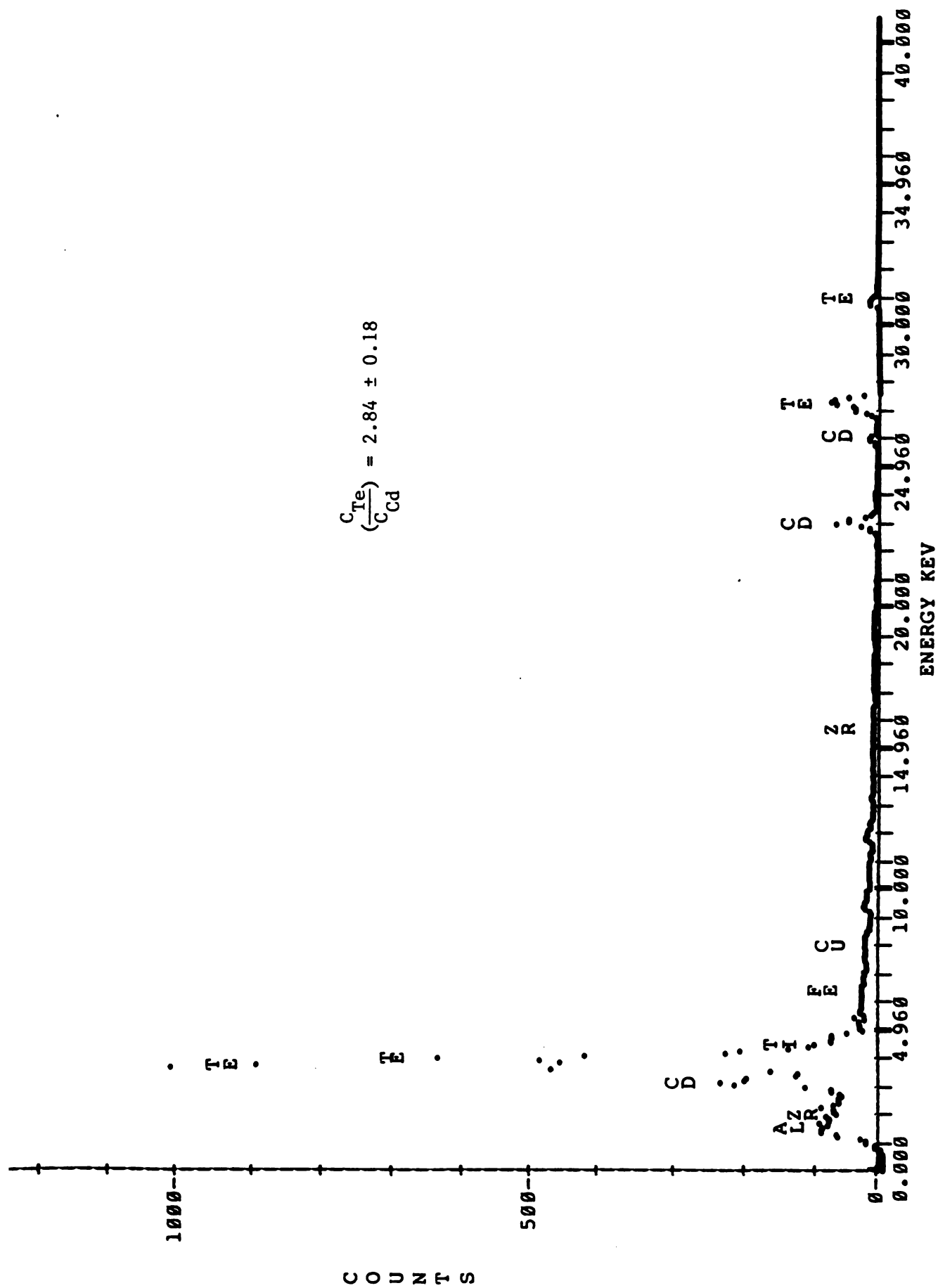


Figure 25. CdTe 3-268 x-ray spectrum of Te deposit shown in Figure 24.

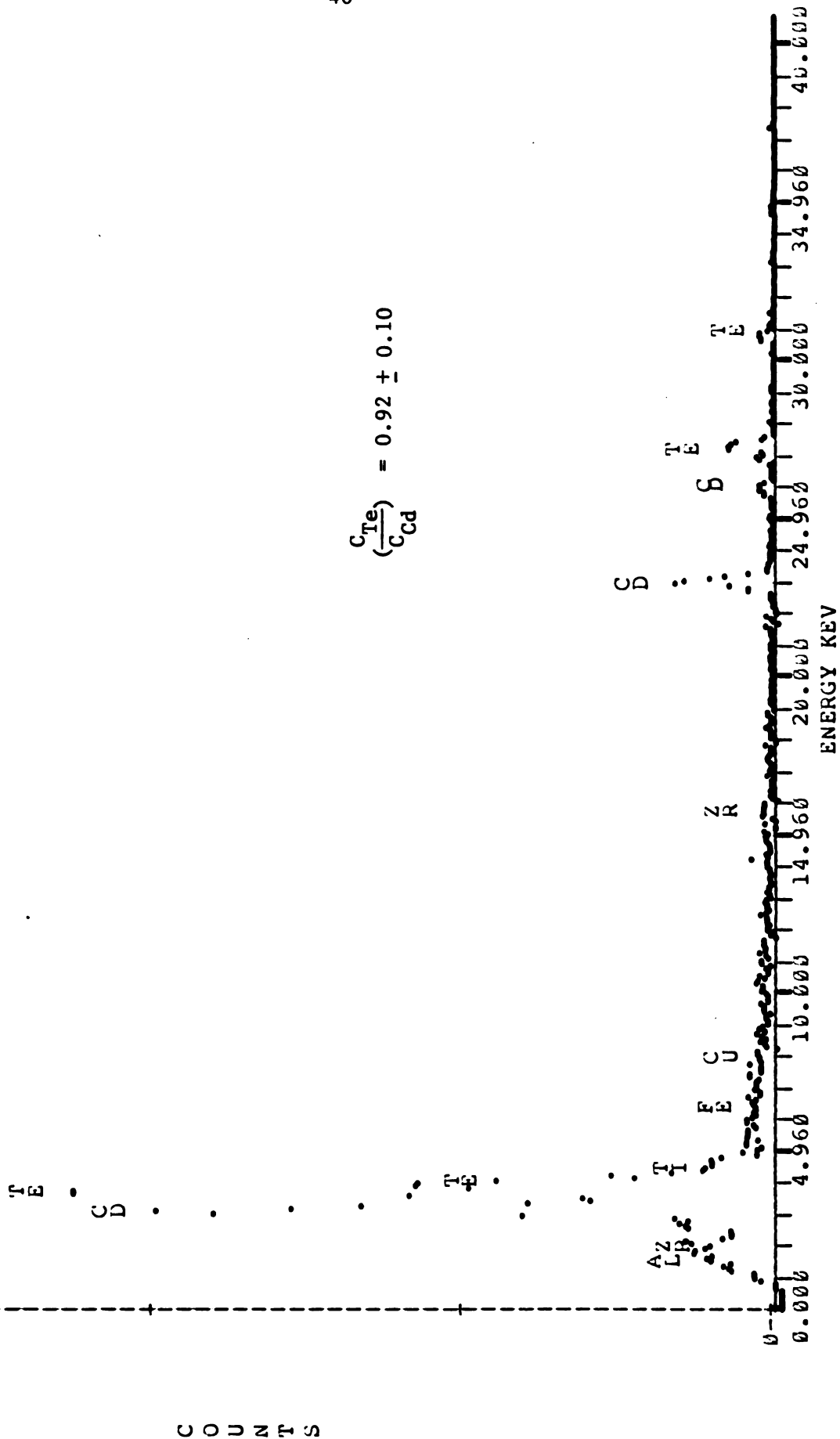


Figure 26. CdTe 3-268 x-ray spectrum of region away from Te deposits.

CdTe 2-36

No distinguishing features such as Te or impurity deposits were seen in CdTe 2-36. Figure 27 illustrates a spot acquired x-ray fluorescence spectrum obtained from this sample. The average weight percent concentration ratio of Te to Cd determined from four such spectra for CdTe 2-36 was found to be 0.84 ± 0.02 .

CdTe 4-2

Deposits of Fe and Zr were found in CdTe 4-2. The Fe deposit shown in Figures 28 and 29 and the Zr deposit shown in figures 30 and 31 were found in the same area. Several other Fe deposits were observed while no other Zr deposits were seen. Figure 32 illustrates a spot acquired x-ray fluorescence spectrum obtained in a region away from impurity deposits. The analyzed samples incurred extensive damage when mounted in the microscope to the point where a meaningful, thin film, average weight percent concentration ratio of Te to Cd could not be obtained. However the ratio from Figure 32 did meet the thin film approximation and was found to be 0.89 ± 0.08 .

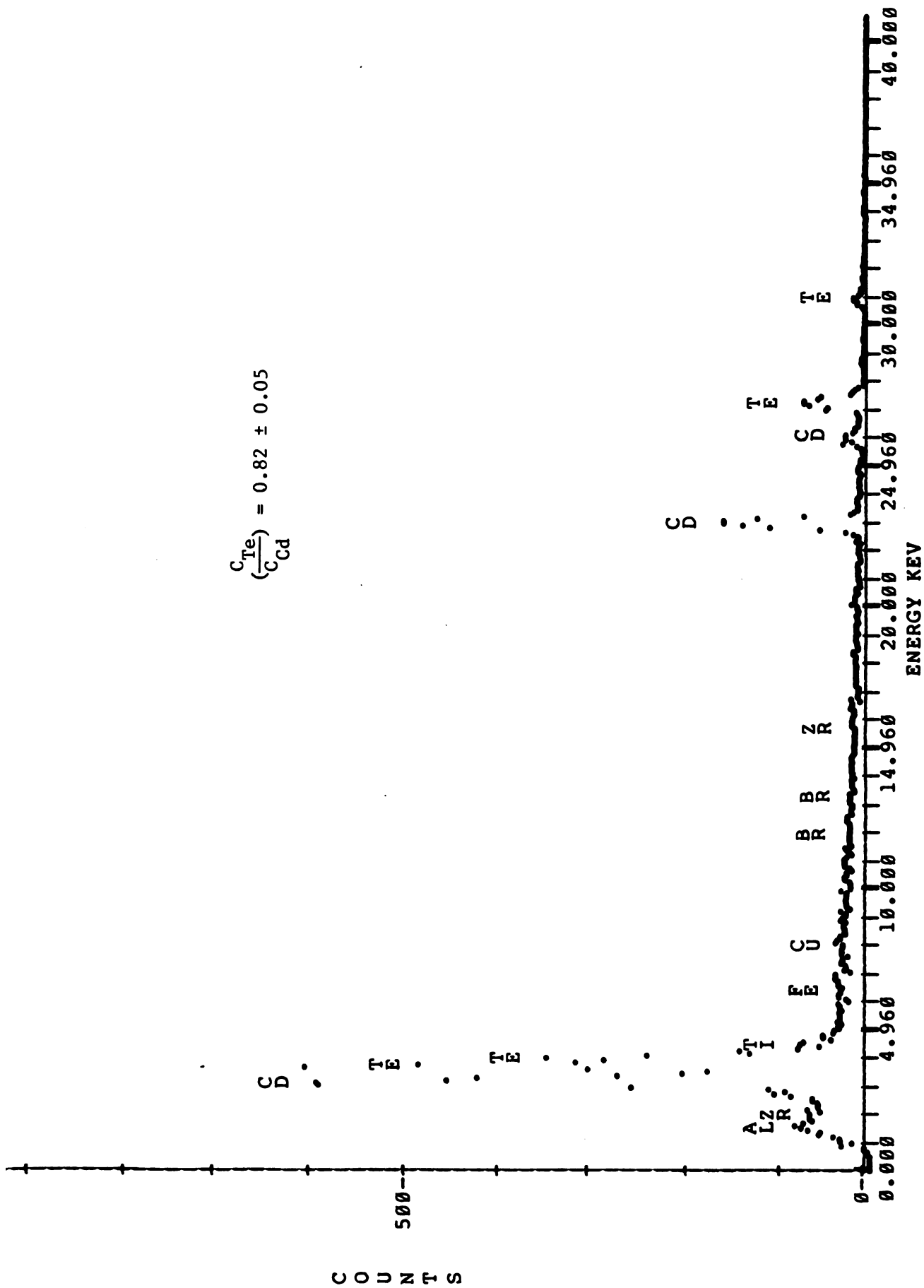
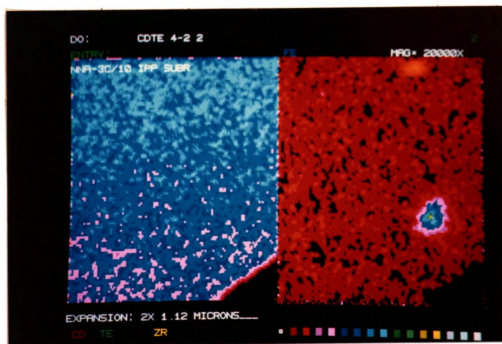


Figure 27. CdTe 2-36 x-ray spectrum of a typical region.



See Figure 29

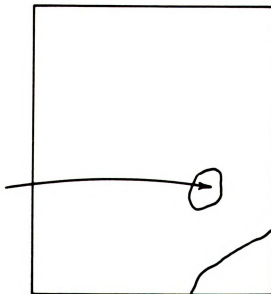


Figure 28. X-ray map of Fe deposit in CdTe 4-2
(Cd map on the left and Te map on the right).

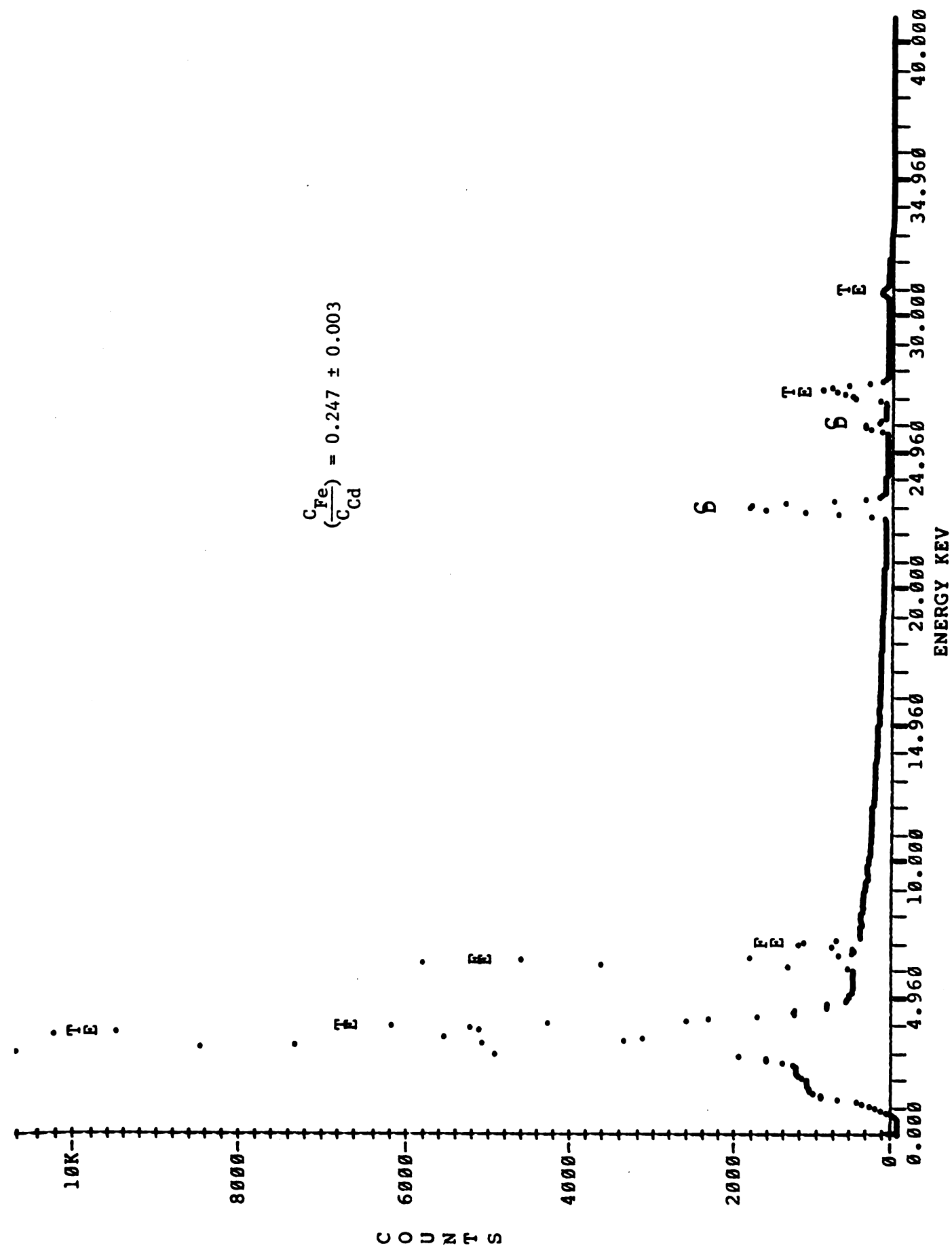
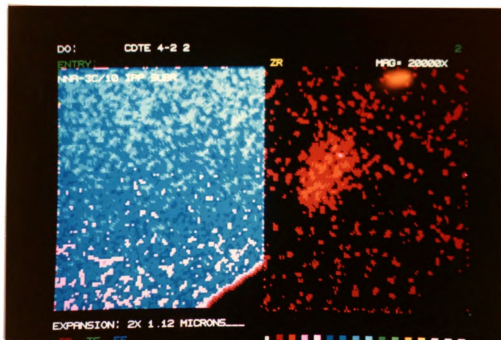


Figure 29. CdTe 4-2 x-ray spectrum of Fe deposit shown in Figure 28.



See Figure 31

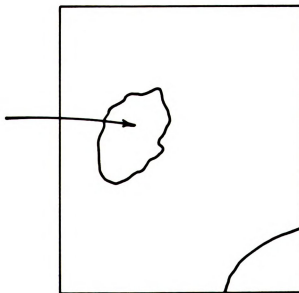


Figure 30. X-ray map of Zr deposit in CdTe 4-2
(Cd map on the left and Te map on the right).

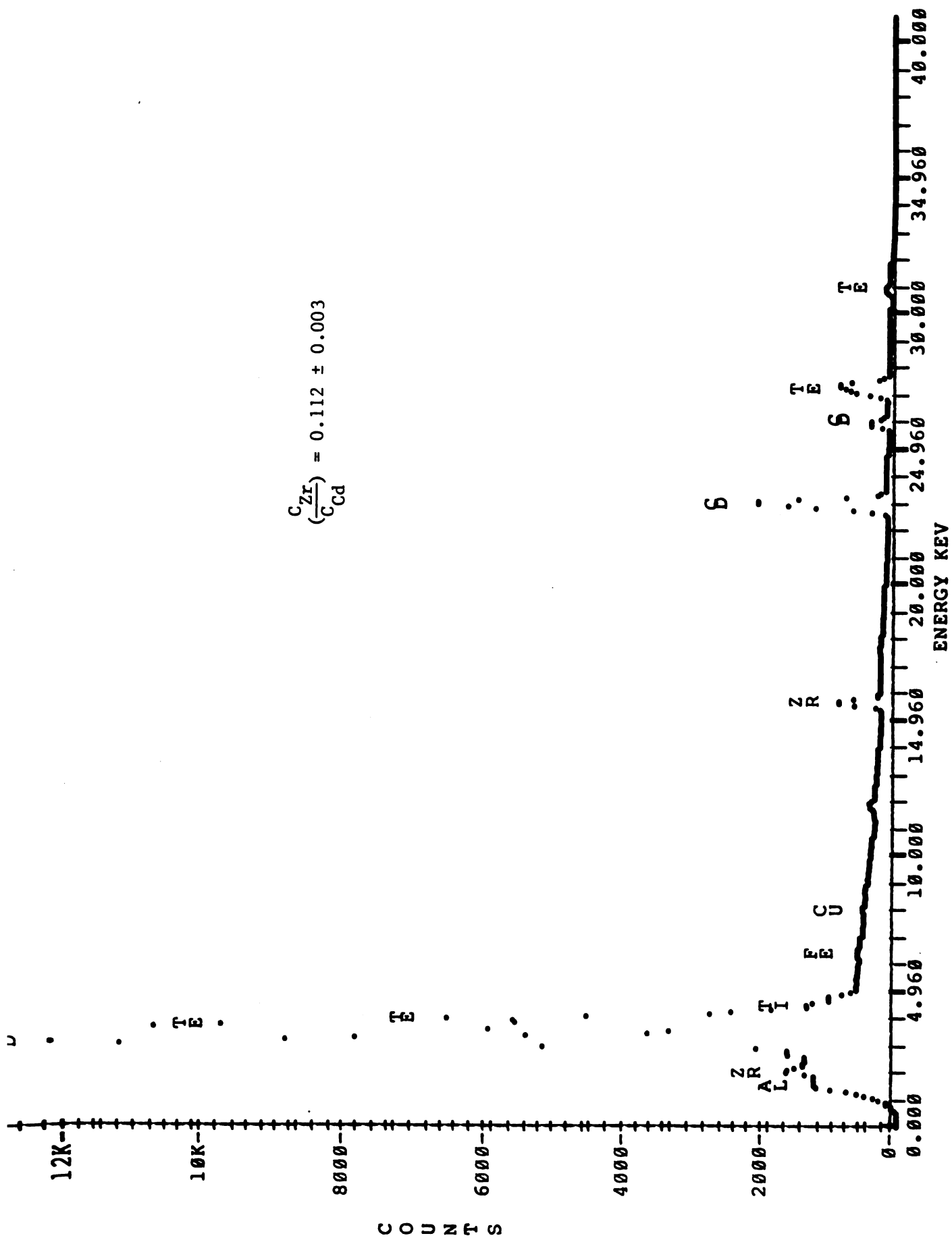


Figure 31. CdTe 4-2 x-ray map of Zr deposit shown in Figure 30.



Figure 32. CdTe 4-2 x-ray spectrum in a region away from impurity deposits.

CdTe 1949

No distinguishing features (such as Te or impurity deposits) were seen in CdTe 1949. Figure 33 illustrates a spot acquired x-ray fluorescence spectrum obtained for this sample. The average weight percent concentration ratio of Te to Cd determined from four such spectra for CdTe 1949 was found to be 0.76 ± 0.02 .

CdTe 3531

No distinguishing features (such as Te or impurity deposits) were seen in CdTe 3531. Figure 34 illustrates a spot acquired x-ray fluorescence spectrum obtained from this sample. The average weight percent concentration ratio fo Te to Cd determined from four such spectra for CdTe 3531 was found to be 0.97 ± 0.05 .

CdTe: Cu 2303

Deposits of Cu and Fe were found in CdTe: Cu 2303 (doped in the melt with $\sim 10^{16}$ Cu). The Cu deposit shown in Figures 35 and 36 and the Fe deposit shown in Figures 37 and 38 were found in the same area; while the Fe deposit shown in Figures 39 and 40 was found in a separate area. Fe traces were always found at Cu deposits; while Cu

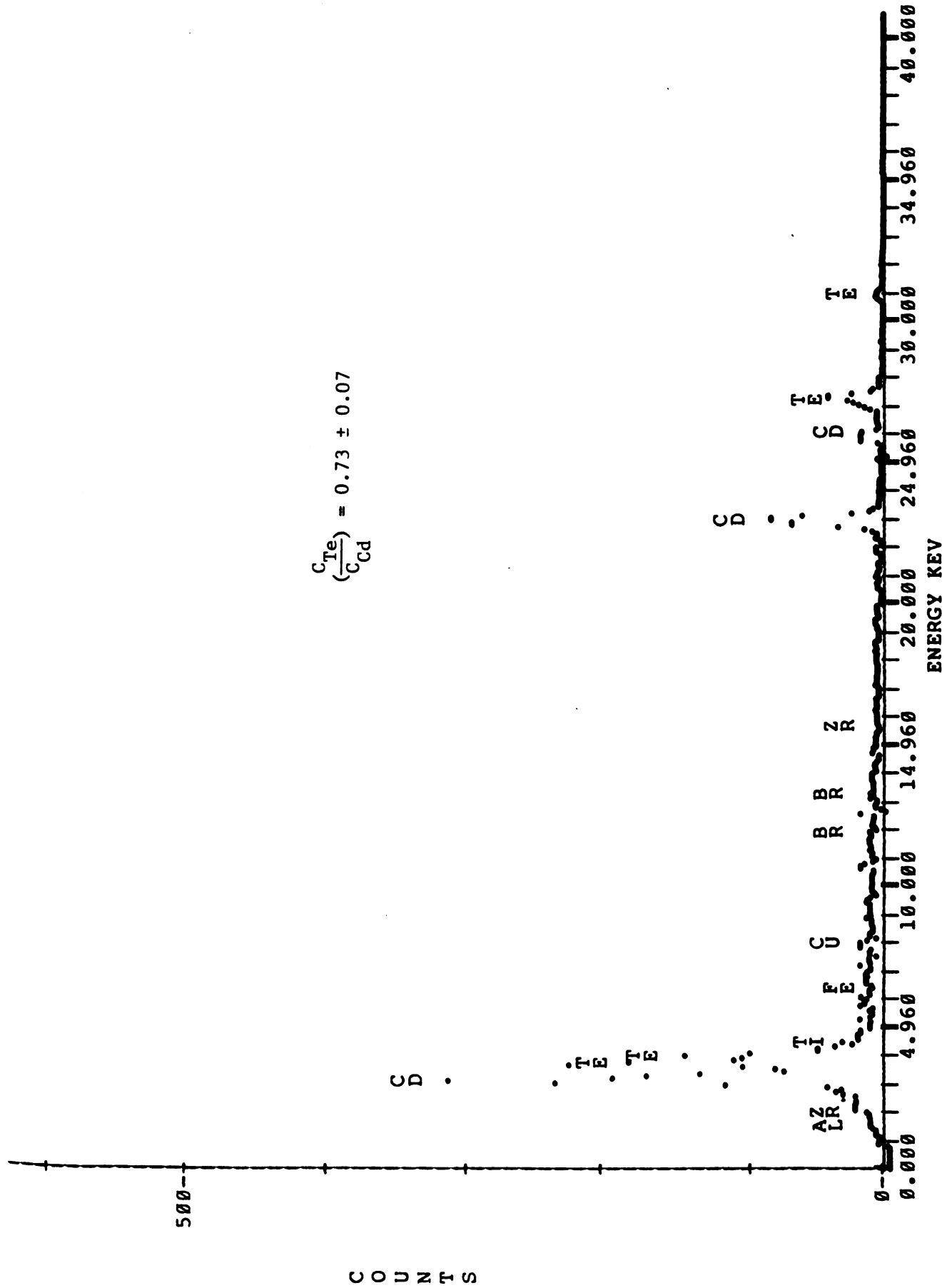


Figure 33. CdTe 1949 x-ray spectrum of a typical region.

$$\left(\frac{C_{Te}}{C_{Cd}} \right) = 0.98 \pm 0.05$$

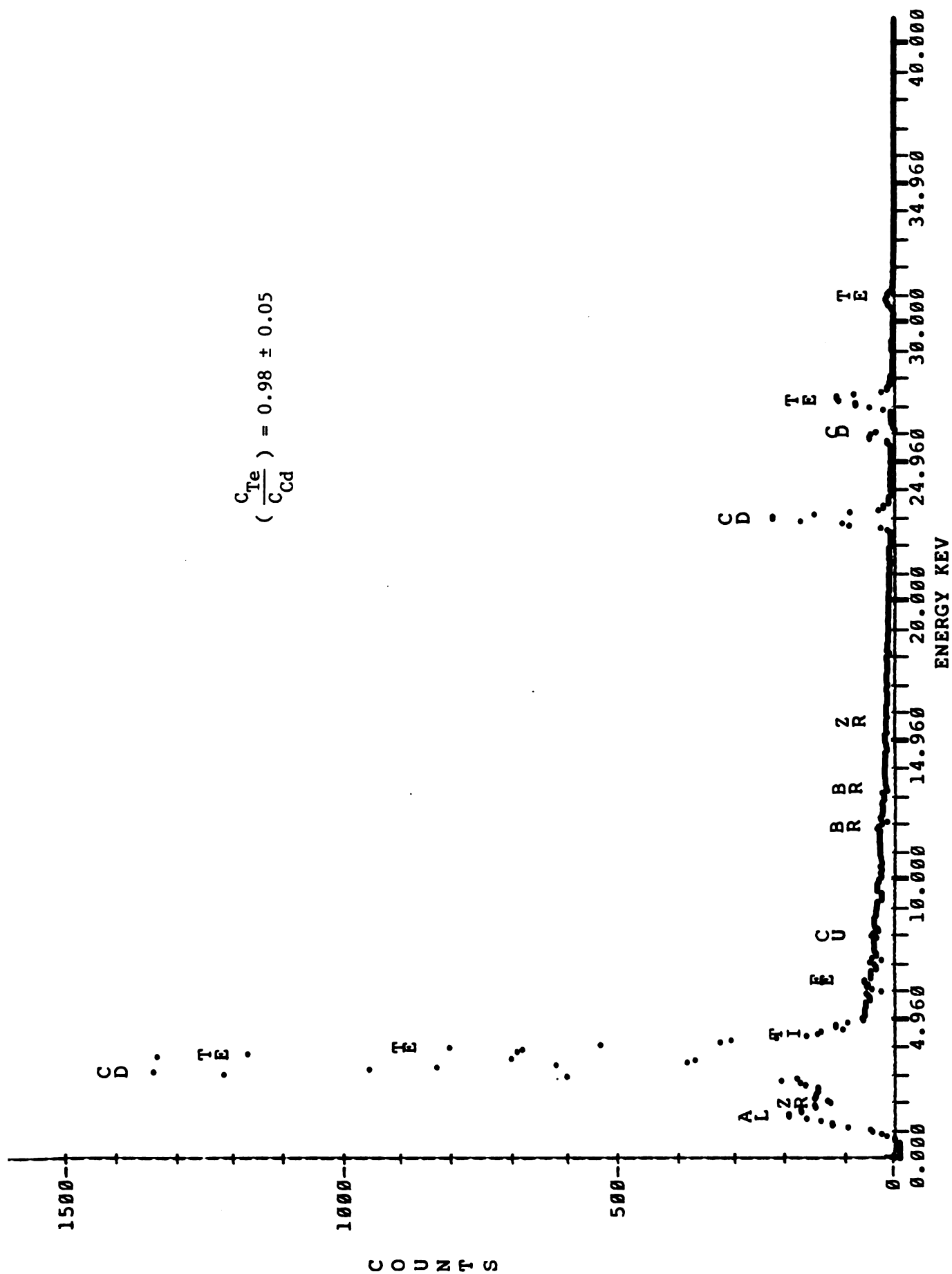
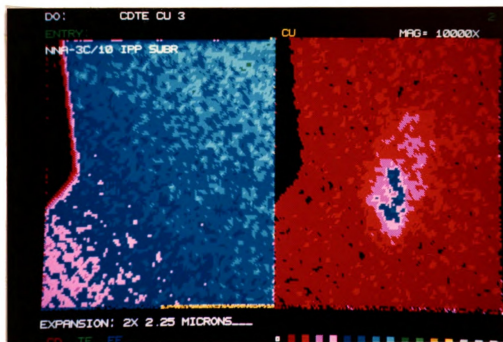


Figure 34. CdTe 3531 x-ray spectrum of a typical region.



See Figure 36

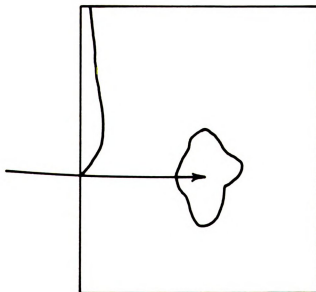


Figure 35. X-ray map of Cu deposit in CdTe: Cu 2303
(Cd map on the left and Te map on the right).

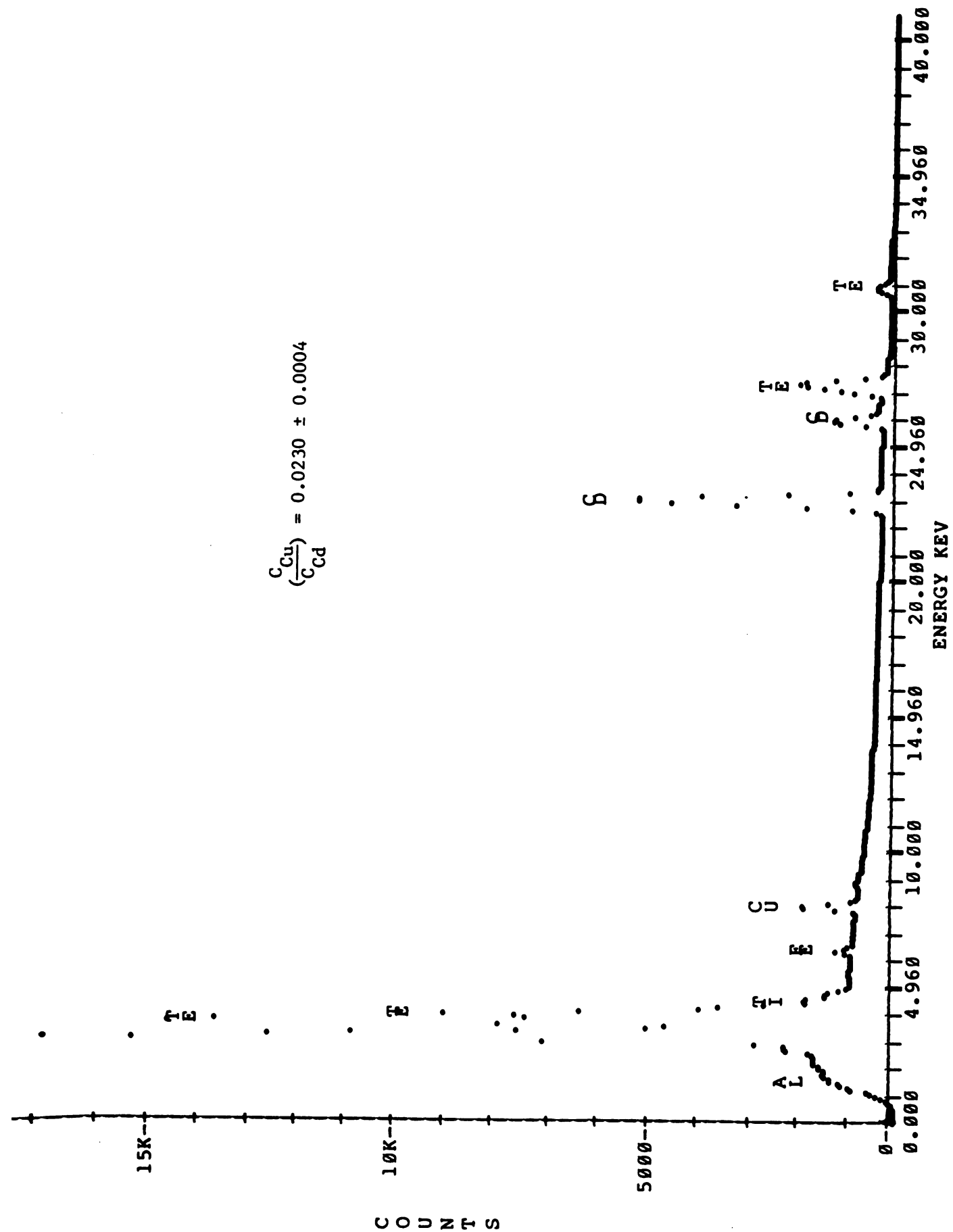
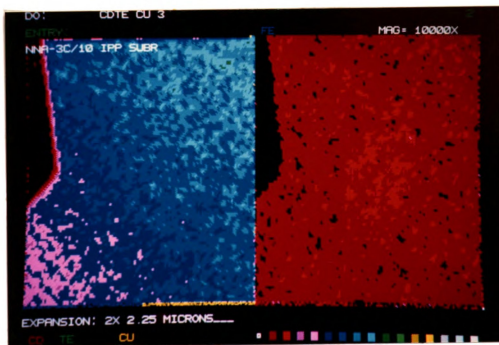


Figure 36. CdTe: Cu 2303 x-ray spectrum of Cu deposit shown in Figure 35.



See Figure 38

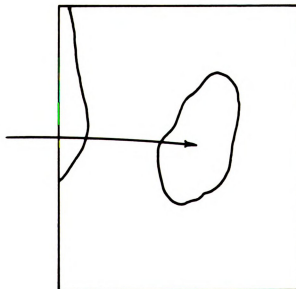


Figure 37. X-ray map of Fe deposit in CdTe: Cu 2303
(Cd map on the left and Fe map on the right).

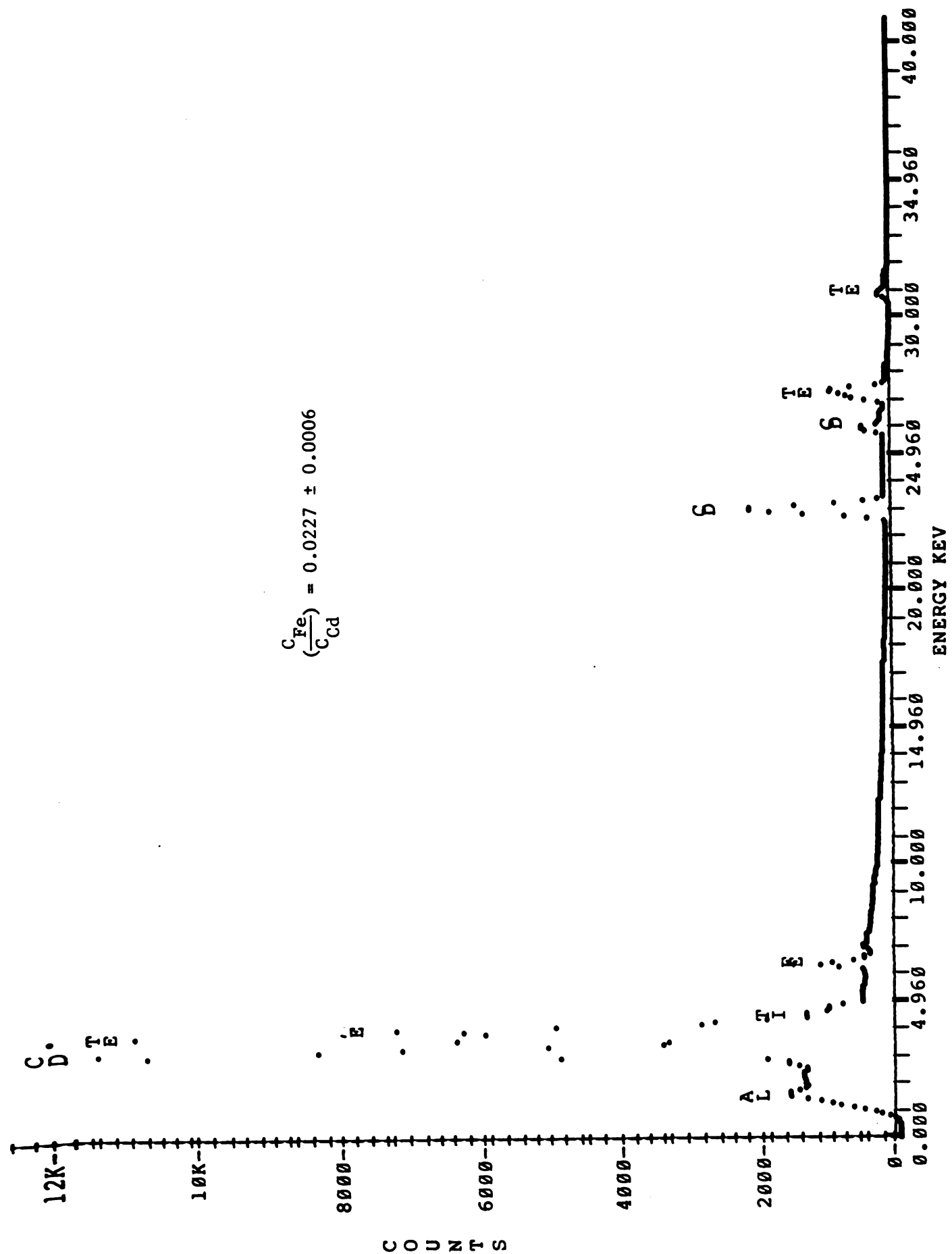
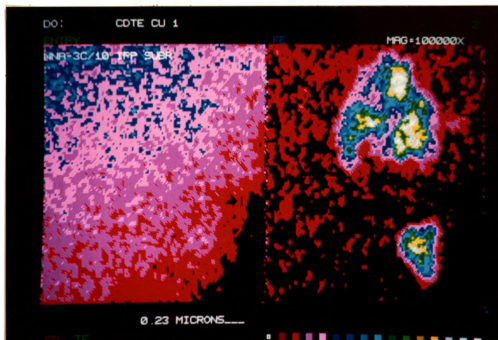


Figure 38. CdTe: Cu 2303 x-ray spectrum of Fe deposit shown in Figure 37.



See Figure 40

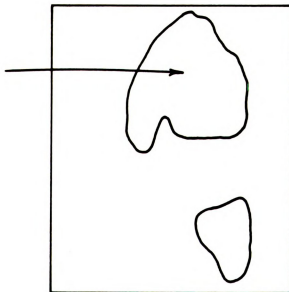
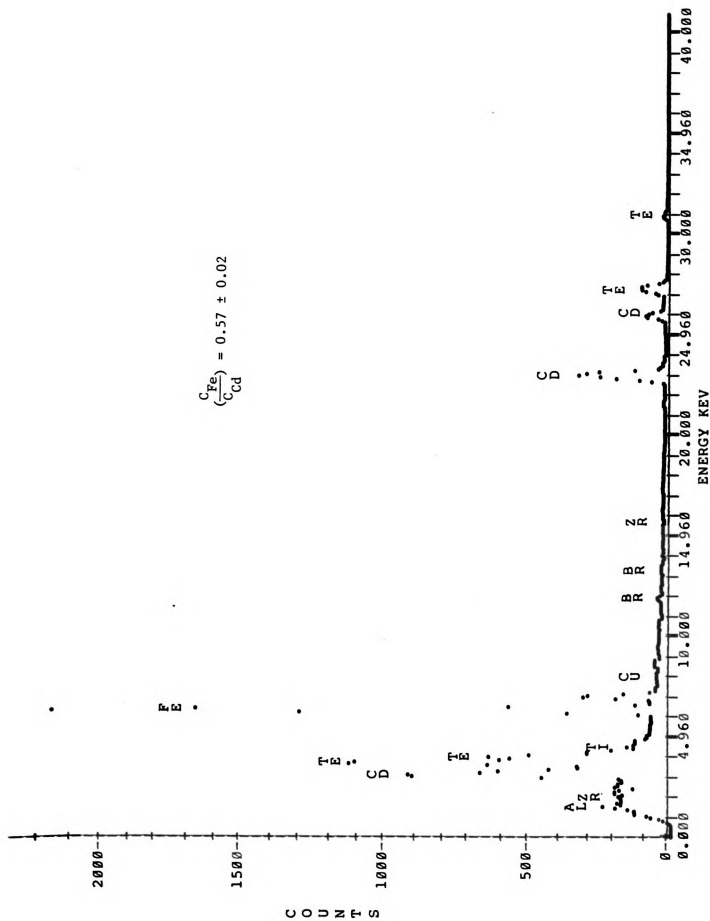


Figure 39. X-ray map of Fe deposit in CdTe: Cu 2303
(Cd map on the left and Te map on the right).



was not found at all Fe deposits. Also, traces of Ti and Al which were unable to be resolved by x-ray mapping were seen as shown in Figures 41 and 42 respectively. Figure 43 illustrates a spot acquired x-ray fluorescence spectrum obtained in a region away from impurity deposits. The average weight percent concentration ratio of Te to Cd determined from four such spectra for CdTe: Cu 2303 was found to be 0.82 ± 0.06 .

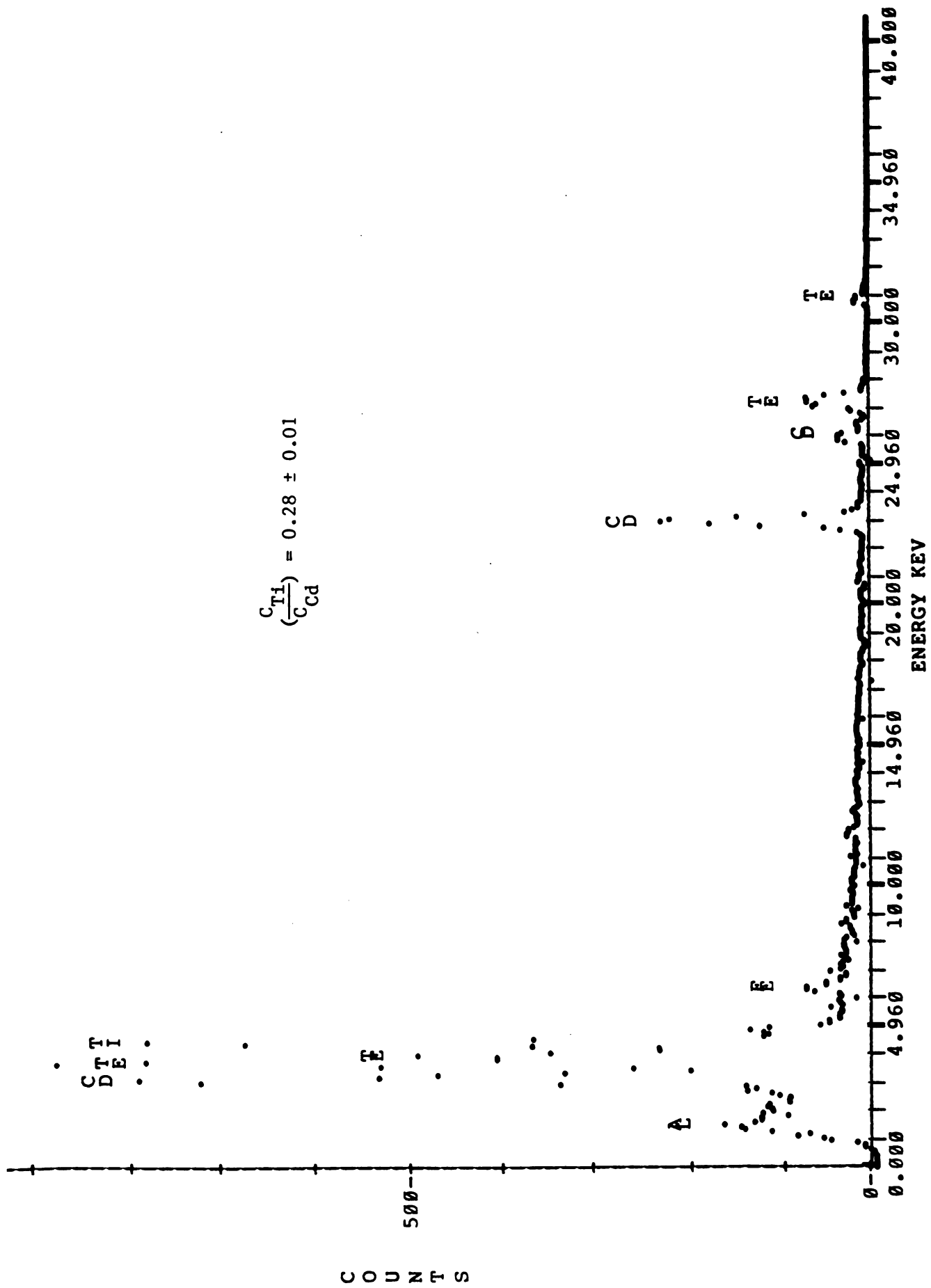


Figure 41. CdTe: Cu 2303 x-ray spectrum of Ti trace.

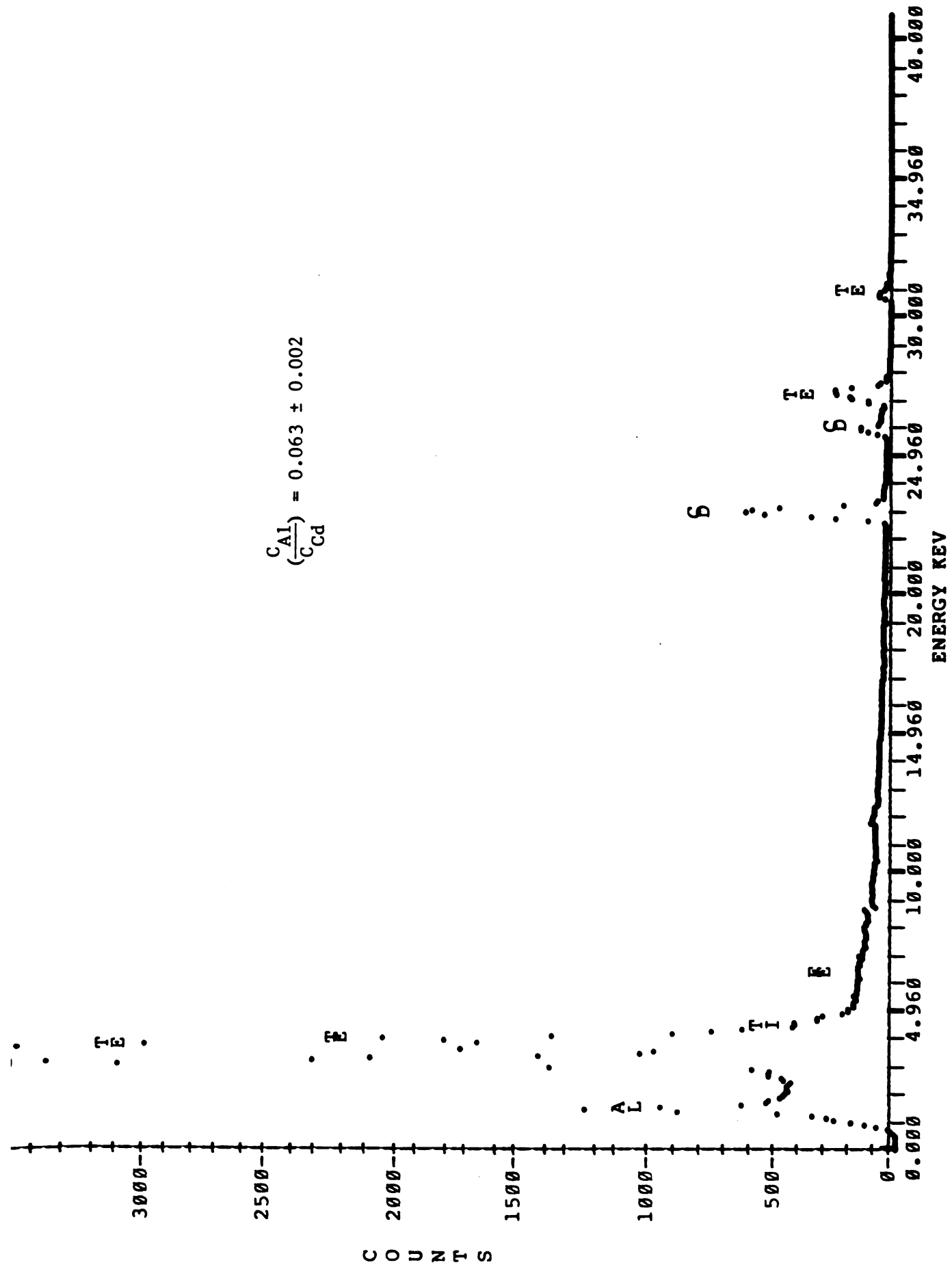


Figure 42: CdTe: Cu 2303 x-ray spectrum of Al trace.

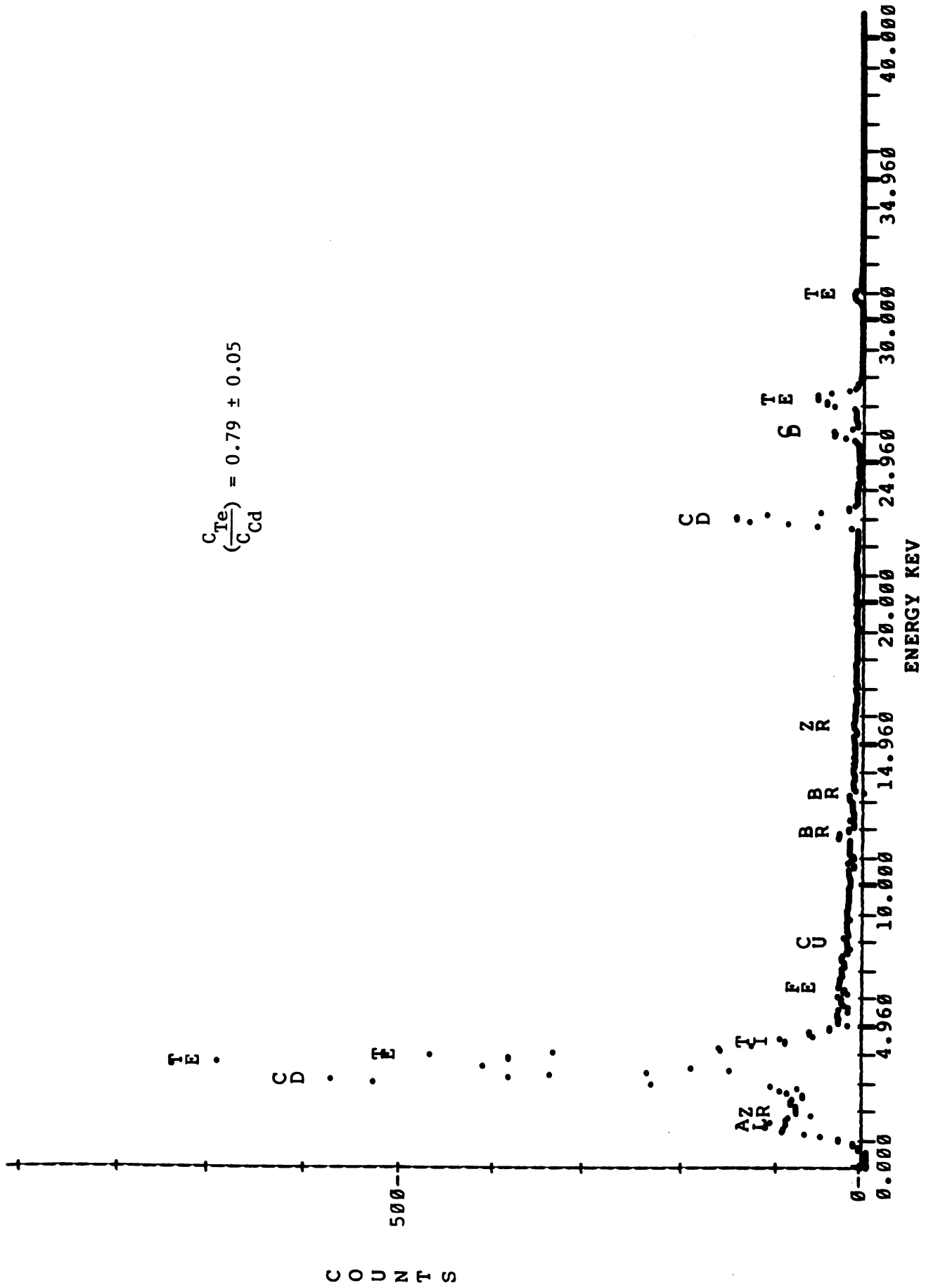


Figure 43. CdTe: Cu 2303 x-ray spectrum of region away from impurity deposits.

V. CONCLUSION

Analysis of CdTe Substrates

Before any meaningful analysis can be done, we need to understand what effects, if any, the chemical etching used in sample preparation has on measured stoichiometry. X-ray fluorescence studies were performed on CdTe 3531 for both etched and cleaved regions. When a sample is mounted in the electron microscope, a substantial amount of damage can result because the CdTe is single crystal and the edges of the perforation are extremely thin. Due to the smoothness or jaggedness of a thin edge seen in the microscope, it is possible to distinguish between etched and cleaved edges. SEM micrographs of both etched and cleaved edges are shown in Figures 44 and 45 respectively. A cleaved edge was chemically etched only on the top surface hence is expected to be representative of CdTe substrates. No chemical difference has been observed between these two types of edges where average weight percent concentration ratios of Te to Cd were 0.92 ± 0.06 for etched regions and 0.91 ± 0.06 for cleaved regions. Thus it seems reasonable to expect our analysis is meaningful in terms of bulk CdTe substrates.

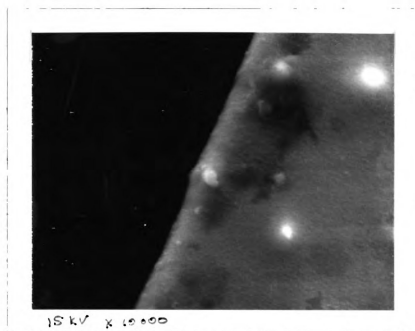


Figure 44. SEM micrograph of etched edge
(magnification= 10,000x)

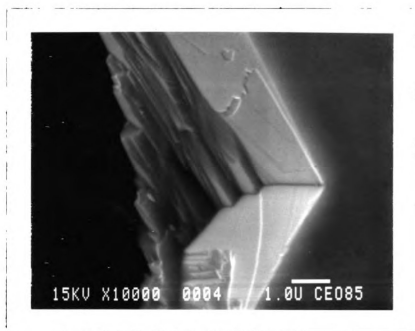


Figure 45. SEM micrograph of cleaved edge.
(magnification= 10,000x)

A list of the six CdTe samples that were analyzed along with the distinguishing features seen and the average weight percent concentration ratios of Te to Cd for regions away from any Te or impurity deposits is shown in Table 2. These CdTe substrates were all expected to be reasonably stoichiometric; however, we observed as much as 20% variation and all samples appear on the Cd rich side. We attribute these Cd rich, nonstoichiometric measurements to a systematic error associated with detector efficiency. No specific information is available for the detector efficiency of our Si(Li) system, hence x-ray fluorescence correction calculations were done for a nominal detector. The Cd and Te K_{α} lines fall on the tail of the efficiency curve as shown in Figure 46; thus, variations in the curve for our system versus a nominal system could be significant. Figure 46 also shows a detector efficiency curve generated by assuming the average weight percent concentration of Te to Cd for CdTe 2-36 to be 1.0. Based on this, our results could be expected to increase by about 10% so that the concentration ratios of the six CdTe substrates would be reasonable. Regardless of the actual weight percent concentration ratios, the difference between samples appears significant.

Our studies of CdTe substrate samples revealed numerous impurity deposits in both doped and undoped substrates. Stoichiometric differences between "good" and "bad" CdTe substrates (in terms of the quality of LPE $Hg_{1-x}Cd_xTe$ grown on them) were also seen.

Table 2. Parameters Characterizing the six CdTe samples.

Sample	Distinguishing Features	Average Weight Percent Concentration Ratio of Te to Cd in regions away from any deposits
CdTe 3-268	Te deposits	0.95 ± 0.05
CdTe 2-36	----	0.84 ± 0.02
CdTe 4-2	Fe and Zr deposits	$0.89 \pm 0.08^*$
CdTe 1949	----	0.76 ± 0.02
CdTe 3531	----	0.97 ± 0.05
CdTe:Cu 2303	Fe and Cu deposits Ti and Al traces	0.82 ± 0.06

*determined from one spot.

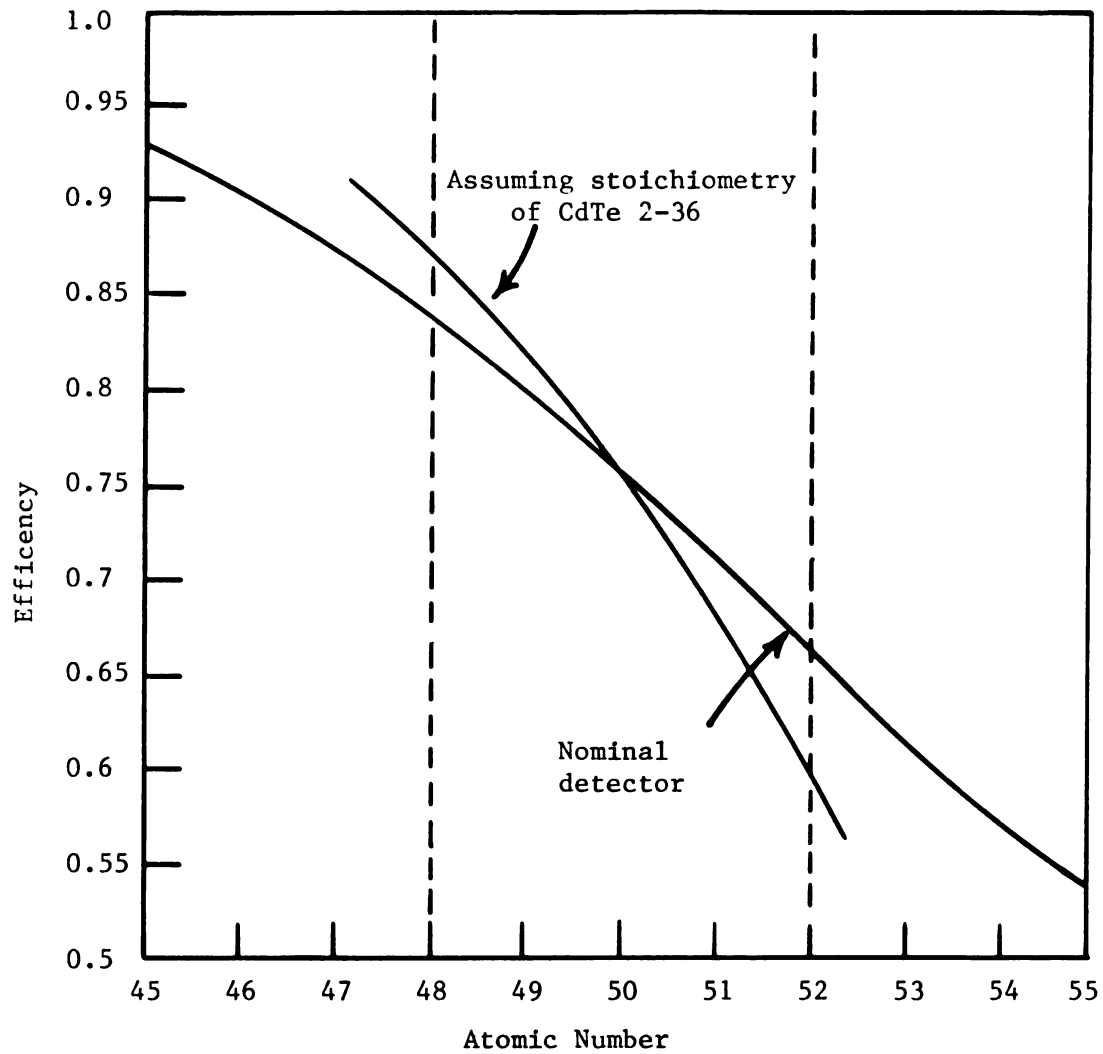


Figure 46. X-ray detector efficiency curves.

Among the Rockwell grown samples, $1000\text{\AA}$ Te deposits were identified in CdTe 3-268, Fe and Zr deposits (approximately the same size) were identified in CdTe 4-2, and no deposits were identified in CdTe 2-36. A 10% variation in stoichiometry was observed between these three samples.

Among the II-VI Inc. grown samples, Fe and Cu deposits approximately $1000\text{\AA}$ in size along with traces of Ti and Al were identified in the Cu doped sample CdTe: Cu 2303. No deposits were identified in CdTe 1949 or CdTe 3531 however a 20% variation in stoichiometry was observed between these two samples - a "good" substrate and a "bad" substrate respectively.

These results should be compared with other optical and electronic analysis performed on the same samples. Such comparisons may lead to a more complete understanding of how CdTe substrates affect infrared detector device performance.

Much work has been done with impurity doped (especially Cu) samples in order to identify the energy levels of the impurity in CdTe. We showed that in a Cu doped sample, significant amounts of Fe were also introduced; hence, any optical or electronic analysis must account for the Fe along with the Cu. In general for any doped (or even undoped) sample, one should investigate the micro-chemistry before any meaningful conclusions are made as to how impurities interact with the host material.

Our work illustrates the capabilities of x-ray fluorescence spectroscopy as a tool for chemical analysis, especially transition metal impurity studies. The Scanning Transmission Electron Microscope can also be used to study defect densities (via bright field imaging) and crystallinity (via micro-diffraction) associated with these impurities; hence it is a powerful and versatile instrument for the characterization of semiconductors important to the infrared detector industry.

Future Work

With our present sample preparation technique it is possible to study the chemistry, crystallography and defects of both substrates and epilayers. By removing different amounts of the epitaxy sample surface during the initial etch, the entire epilayer, the epilayer-substrate interface, and several depths of the substrate itself can be studied. Such experiments should be performed for substrates with and without epilayers to develop a better understanding of epilayer-substrate interactions in terms of defect propagation and impurity diffusion. Comparing these results with optical and electronic analysis performed on the same materials would provide a rather detailed understanding of infrared, semiconductor detectors.

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APPENDIX A

CdTe Electron Microscope Sample Preparation: Step-By-Step Procedure

- 1) Start with a bulk piece of CdTe approximately 7mm square and about 600 μm thick. Place the CdTe piece, top surface up, in a small dish of 2% Br/MeOH solution for 4.5 minutes. Remove it and rinse it thoroughly in methanol. This etches away the top 25 μm to remove any mechanical defects, leaving a clean surface of CdTe. Place the CdTe piece on a filter paper in a covered petri dish to keep it clean. Be careful not to handle the CdTe with hands or metal objects. Any transferring of the sample should be done with clean plastic tweezers.

- 2) To mount the CdTe on the 3000 rpm spinner, place and trim a piece of double sided tape on the spinner platform. Now center the CdTe piece, top-surface up, on the spinner platform and apply a small amount of pressure to the corners to secure to the tape. Be careful not to touch the center area of the sample.

Turn off all lights and turn on a yellow safety light to protect the photoresist. Turn on the spinner and apply a drop of Shipley 1375 photoresist at the center of the CdTe piece.

Let the spinner run for about 30 seconds and repeat the photoresist application until the surface of the CdTe takes on a reddish tint. This may take as many as 4 to 5 repetitions depending on temperature and humidity conditions. Using plastic tweezers, carefully remove the CdTe piece and place it on a teflon slide to dry. Once completely dry, clean any excess photoresist off the back side using acetone and a Q-tip. Be very careful not to let any acetone touch the front side. Return the sample to its petri dish. Again remember to do all undeveloped photoresist work in a yellow light environment to prevent premature development.

- 3) Mount a 250 watt ultraviolet flood light on a ring stand about one foot off the base. Let the lamp warm up for 10 minutes. With the photoresist side of the CdTe piece up in an uncovered petri dish, place the photoresist mask, disc side down, on the sample and center one complete disc. It has been determined that the best results are obtained when only one disc is exposed per sample. Place the assembly under the flood lamp for 5 minutes. Remove the sample and develop it in a small beaker of Shipler Microposit 351 developer which has been diluted by 50% with distilled water. Use a slow agitating motion until the disc is clearly visible and the surrounding area is shiny (about 17 to 20 seconds). Rinse the disc thoroughly in distilled water. Examine the disc carefully to inspect for a clean, well shaped disc. If the disc is not satisfactory, strip it with acetone and return to step 2. When

a satisfactory photoresist disc is obtained, the room lights can be turned on and the CdTe piece can be returned to its petri dish.

- 4) Obtain a small dish and fill it with a 4% Br/HBr solution. HBr is used to protect the photoresist mask which is soluble in methanol. Place the masked CdTe sample face up in the covered dish. Let the sample etch for 1 hour and 15 minutes. Remove the sample and rinse it in distilled water. This etching step produces a plateau which should be ~150 um in depth as was shown in Figure 17. Measure the plateau with an appropriate depth gauge and re-etch if necessary to obtain the proper dimension. Once etching is complete, strip off the photoresist with acetone and return the CdTe piece to its petri dish.

- 5) Remount the CdTe sample, plateau side up, onto the spinner. Plug the spinner into a variac and set on a slow speed. Under yellow light, apply a thick coat of photoresist to completely cover the CdTe piece. Remove the sample and let it dry on a teflon slide. This may take several hours as the photoresist coat is thick. Once the sample is dry, clean the back side using acetone and a Q-tip. Now paint a very narrow bead of photoresist onto the sides and back edge of the sample in order to protect it while etching off the back side (see Figure 47). If this step is not taken, the disc will not have the chance to emerge with a well formed shape. This should all

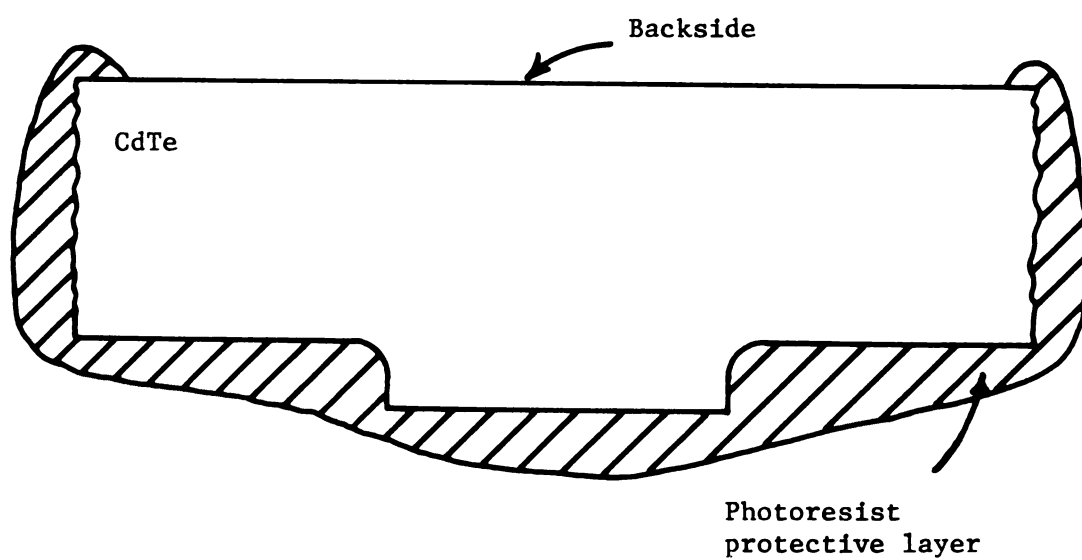


Figure 47. CdTe piece with photoresist protective layer prior to semistatic backside etching.

be performed on the teflon slide. The photoresist will bleed under, to the top side. Once the edges are dry, turn the sample over and allow the top to dry. After all the photoresist is completely dry, develop in a 50-50 solution of developer and distilled water and return to its petri dish.

- 6) Fill a medium sized dish with a 4% Br/HBr solution and place it on a magnetic stirring plate. Plug the plate into a variac and turn it on. Put a small stirring "peanut" in the dish and set to the slowest possible stable speed. Now center a teflon basket (see Figure 48) in the dish and place the sample face down in the center of the basket. Cover the dish with a watch glass and let the back side etch until the CdTe disc can be retrieved. This will take 6 to 9 hours. Remove the sample and clean it thoroughly in distilled water. Place the sample on a filter paper and strip off the photoresist with acetone. Using vacuum tweezers, put the disc on a clean filter paper and return it to the petri dish.

- 7) Follow the chemical thinning procedure in the manual to set up and tune the South Bay model 550C jet thinner. Use a 10% glycerol, 0.5% Br in methanol etching solution. Remove the sample holder and secure a mylar disc to it with a thin ring of Apiezon M grease. Take care not to block the light sensor hole of the holder. The vacuum tweezers can be used to manipulate the mylar disc into place. Now place the CdTe disc, back side up in the center of the holder on top of the mylar disc and

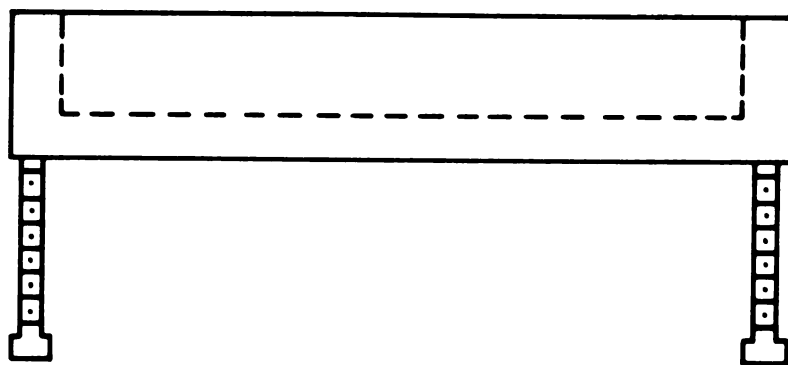


Figure 48. Teflon basket used to hold CdTe piece during semistatic backside etching.

cover the sides with grease. Leave the center portion of the sample uncovered as shown in Figure 49. It is desirable to cover all but the center 1mm of the CdTe disc in order to seal the sample from the etchant and define the thinning region to insure a well formed dimple.

- 8) Mount the holder assembly into position on the jet thinner and activate the automatic sensor mode. The trigger level is quite sensitive; however, very nice results can be obtained once a feel for the apparatus is obtained. When the sensor turns off the jet stream, remove the sample holder assembly and rinse it in methanol. Examine the assembly intact under a light microscope for a perforation in the CdTe. Repeat the jet thinning until a microscopic perforation is obtained. Now dissolve the grease with toluene.
- 9) Submerge the top of the sample holder in toluene. Remove the CdTe and mylar discs from the holder by poking a needle through the back of the holder. Slide the mylar disc off the CdTe disc with care and retrieve the sample from the toluene bath using vacuum tweezers. Put the sample on a clean, small filter paper and submerge it in a warm bath of methanol for 30 minutes. Note that it is wise to have a large filter paper in the bottom of the bath. Be very careful with the CdTe sample as the edge of the perforation is only 1000⁰Å thick and very

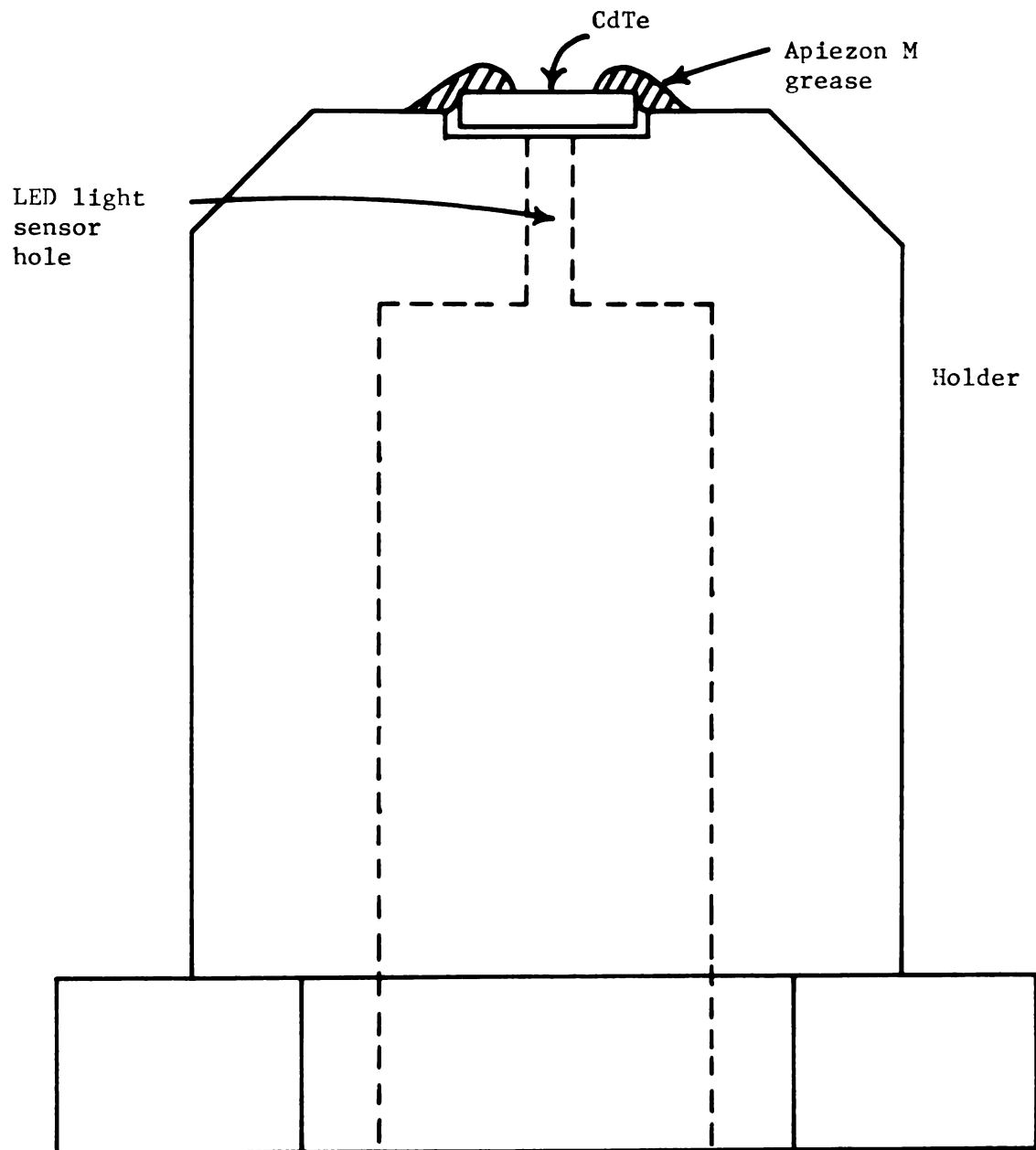


Figure 49. CdTe disc mounted with Apiezon M grease on holder for South Bay model 550C jet thinner.

fragile. Remove the CdTe disc and transfer it to a clean filter paper. The sample is now ready to be mounted in the microscope.

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