

ASD-TDR-63-310

**FOREWORD**

This report was prepared by the Physics Laboratory. The work was initiated under Project 7360, "Materials Analysis Evaluation Techniques," and Task 736005, "Compositional, Atomic, and Molecular Analysis." It was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, with W. L. Baun acting as project engineer.

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The authors wish to thank Mark Goldschmidt for help with experimental work.

# *Contrails*

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**ABSTRACT**

Long spacings and physical properties are shown for a number of metallic salts of n-aliphatic acids. Among the salts made are those of thallium, copper, lead, zinc, uranyl radical, iron, cobalt, nickel, magnesium, and the more soap-like members such as sodium, potassium, lithium and calcium. Spacings ranged from about 15 Å to 40 Å for the salts measured, which is of the correct size for use as a dispersing device in the X-ray spectral region 15 to 60 Å. Some salts were found to have properties which negated their use as dispersing devices for X rays, while others were found to be potentially good analyzing crystals or three dimensional gratings. Of the compounds prepared, zinc, thallium and uranyl salts showed promise for use as dispersing devices for long wave X rays. Almost any desired long spacing may be obtained with the right combination of metal and acid, and these spacings may be calculated once a group of three or more salts of a homologous series has been prepared. Results on some aromatic compounds such as monovalent metal salts of phthalic acid are discussed. These compounds show promise for use as single crystal analyzers for soft X rays. Soft X-ray spectra are shown using a layered barium stearate film on glass and potassium acid phthalate as analyzers.

This technical documentary report has been reviewed and is approved.



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## INTRODUCTION

Although the region of the X-ray spectrum between 15 and 60 Å is of considerable interest to solid state spectroscopists, it is beset with experimental difficulties that make routine measurements in this spectral region almost impossible. Nearly all of the problems of this region arise primarily because of the high absorptivity of X rays of long wavelength. Excitation, detection and dispersion problems plague the worker in this region. Normally, considerations of vacuum to alleviate absorption problems can be worked out, and radiation may be obtained either from primary excitation using electrons or secondary excitation using a soft X-ray source. Further, recent work (ref 5) on detection systems indicates that a flow counter with a thin cellulose nitrate window is quite efficient at wavelength near 50 Å. A windowless magnetic strip amplifier made by Bendix (ref 4) shows promise for use in this region but is not energy dependent, thus making pulse height analysis impossible using this detector (ref 2). Recent work with the detector in this laboratory shows this counter to be very insensitive in the 5-15 Å region.

As yet, however, no straightforward solution has appeared to solve the dispersion problem. A concave grating has been used (ref 12) but in this region the energy resolving power is quite small. Karlsson reports the use of some aliphatic acids and some lead salts (ref 6). Although most of the organic acids, hydrocarbons, etc. that have been considered have sufficiently large interplanar or packing distances to disperse X rays in this region (d value at least one-half of wavelength to be measured), they usually suffer from poor mechanical properties, low melting point, and high vapor pressure. In order to be of any use most of these crystals must be cooled to retain a stable configuration under vacuum. The desired objective would be to retain the large spacing and preferred orientation (001) properties of long-chain aliphatics while increasing the melting point and enhancing mechanical properties.

Formation of metal salts of aliphatic and aromatic acids appears to fulfill the objectives of orientable, large crystal spacings and relatively high melting point. The purpose of this report is to survey some of the possible compounds which may show promise for use as dispersing elements for long wavelength X rays, either as single crystals or as polycrystalline oriented films.

## EXPERIMENTAL

## Preparation of Salts

Metal salts of saturated fatty acids are exceedingly easy to prepare and may be prepared from a number of starting metal compounds. The easiest reaction and one least likely to introduce impurities is the direct reaction of acid and metal to form the metal salt plus hydrogen. The product is pure and need only be washed with an organic solvent such as acetone to remove excess acid if present. The reaction may be carried out at room temperature with liquid acids (up to C<sub>10</sub>, decanoic) and with only sufficient heat to melt the acids for the solid members. Naturally the reaction is accelerated with moderate heating of the mixture even when liquid acids are used. Another method of preparation that was used when larger quantities were desired, or when pure metals were not available, was the reaction of a metal acetate with a saturated acid to form a metal salt plus acetic acid. Since nearly all the salts are insoluble in water, the acetic acid may be removed easily by washing or it may be volatilized by heating. Metal hydroxides plus the acid make another useful preparation with only water formed in addition to the salt. Some metal chlorides, bromides and carbonates also give the desired product, with easily removed by-products. Thallium salts were prepared from thallos bromide.

## Apparatus

The Philips\* diffractometer was used to record diffraction patterns of the long-chain metallic salts. Beam defining slits of from 1/6 degree to 1 degree were used, according to the angular region being scanned and the degree of resolution desired. Nickel filtered copper radiation was used along with a scintillation counter detector. Pulse height analysis was not employed. The diffractometer was aligned using first a silicon standard and then the spacings were checked from a thin film of the stable form of stearic acid. The alignment was also checked using the 33.6 Å line of cholesterol as suggested by Kittrick (ref 7). Although the diffractometer was well aligned at low angles, long spacings were calculated from an average of the highest orders recorded. In one case as many as 21 orders were observed. Samples were prepared by grinding the salts in a mortar and placing them on a ground glass slide. In addition, some long spacings were measured by melting the salt on a ground glass slide. It was found that a ground glass base enhanced preferred orientation in the long spacing direction and gave a more uniform layer of salt. This technique was followed with the same effect by Ohlberg (ref 10) in a study on long-chain paraffins.

Melting and freezing points on aliphatic compounds were taken on a Fisher-Johns melting point apparatus under a binocular microscope. Melting points for aromatic compounds were determined by Huffman Microanalytical Laboratory.

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\*Philips Electronics, Inc., Mt. Vernon, New York.



DISCUSSION AND RESULTS

Aliphatic Compounds

Long chain organo metallics have several advantages over pure hydrocarbons in consideration for use as long-wave X-ray dispersing devices. First, the insertion of a metal in the lattice should increase the scattering power of the crystal. Perhaps the greatest scattering power could be gained from a monovalent metallic ion in the lattice but few heavy monovalent metals exist. Second, the melting point of the metal salt is much higher than the acid or the corresponding hydrocarbon. Third, and probably most important, is the greater overall stability of the metal salt.

With the advantage of added scattering power in mind, long-chain salts of a heavy metal, lead, were prepared. Lead salts are among the easiest to prepare from the metal itself and give intense diffracted reflections. Melting points range from 72°C for lead hexanoate (C<sub>6</sub>) up to 106°C for lead decanoate (C<sub>10</sub>). Although these melting points are relatively low they are considerably better than pure hydrocarbons of the same spacings. Table 1 lists some of the lead salts prepared along with their spacings. The long spacings in table 1 agree fairly well with film work done by Trillat (ref 13).

TABLE 1  
LONG SPACINGS AND MELTING POINTS FOR LEAD SALTS OF  
n-FATTY ACIDS

Compound*	Spacing, Å	Approx. M. P., °C
Pb-C <sub>6</sub>	20.42	72
Pb-C <sub>7</sub>	23.11	84
Pb-C <sub>8</sub>	25.57	102
Pb-C <sub>9</sub>	27.55, 28.30	105
Pb-C <sub>10</sub>	30.00, 30.69	106

Spacings shown in table 1 are those formed at room temperature. Polymorphism is quite prevalent in lead soaps and up to four other spacings than those given can result when the reaction is carried out at higher temperatures or the room temperature phase is melted. Because of this tendency toward forming more than one phase, melting and solidification points are difficult to observe and therefore are reported only approximately.

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\*Notation C<sub>n</sub> will be used throughout paper and refers to the total number of carbon atoms in the compound. The complete formula for these compounds is M(C<sub>n</sub>H<sub>2n-1</sub>O<sub>2</sub>)<sub>2</sub>.

Figure 1 shows diffractometer traces which depict three different polymorphic tendencies in lead salts. In the top trace lead heptanoate shows the formation of two new phases upon heating to the melting point. In the next pattern, lead octanoate forms one new phase in addition to the original form. In the bottom pattern two completely new forms of lead nonanoate are formed in place of the original two phases present in sample as precipitated from solution. From these traces it can be seen that a polymorphic series such as lead salts would be rather difficult to use as dispersing devices for long-wave X rays.

Copper salts of the same acids used with lead, hexanoic through decanoic, were prepared and gave long spacings ranging from 17.0 Å for Cu-C<sub>6</sub> to 27.7 Å for Cu-C<sub>10</sub>. The compounds form a homologous series since the long spacing can be plotted against the number of carbon atoms present giving a resultant straight line. Melting points are higher than in lead salts. However, the copper salts are more difficult to prepare and crystallize and have a tendency to hydrate. Overall physical and chemical properties of copper salts are not favorable for use as dispersing devices. It is possible, however, that salts or soaps of higher acids (C<sub>12</sub> to C<sub>18</sub>), with melting points of about 110 to 125°C, could be used as dispersing elements. This series was not investigated since predicted spacings for these compounds were larger than was desired for the region 15 Å to 60 Å.

Uranyl salts, formed from uranyl acetate, are among the most promising compounds prepared. Table 2 shows a representative group of these compounds, along with the long spacings and melting points.

TABLE 2  
LONG SPACINGS AND MELTING POINTS OF SOME LONG CHAIN  
URANYL COMPOUNDS

Compound	Long Spacing	Melting Point, °C
UO <sub>2</sub> -C <sub>6</sub>	14.60	> 243
UO <sub>2</sub> -C <sub>8</sub>	19.13	222
UO <sub>2</sub> -C <sub>9</sub>	21.75	207
UO <sub>2</sub> -C <sub>18</sub>	37.80	118

These salts are easily prepared, are quite stable, do not hydrate, and as can be seen from table 2, have very high melting points. Uranyl octadecanoate, although having a spacing larger than necessary for the spectral region of interest, is included in table 2 especially to show the sharp decline in the melting point curve as carbon atoms are added.

Zinc salts of saturated fatty acids also showed promise for use as analyzing devices for long-wave X rays. Zinc salts were prepared with ease from both the metal and the acetate, and showed good stability and resistance to hydration. The zinc salts were found to be polymorphic, but not nearly to the degree that lead salts were. Table 3 lists zinc salts of the same acids shown for lead, along with long spacings (room temperature, and after melting), and melting points. These salts, along with most of the others prepared,

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could be oriented by working, melting, or depositing them from solution on a suitable substrate, so that no reflections due to side spacings could be recorded.

**TABLE 3**  
LONG SPACINGS AND MELTING POINTS FOR SOME ZINC SALTS OF  
n-FATTY ACIDS

Compound	Long Spacing, R.T., Å	Long Spacing after Melt., Å	M.P., °C
Zn-C <sub>6</sub>	16.08	16.31	144
Zn-C <sub>7</sub>	18.45	18.60	139
Zn-C <sub>8</sub>	20.85	No change	136
Zn-C <sub>9</sub>	23.33	No change	131
Zn-C <sub>10</sub>	25.02	25.84	137

Salts of a heavy monovalent metal, thallium, were prepared and found to be quite useful in the region of interest. However, C<sub>6</sub> to C<sub>9</sub> homologs were difficult to prepare and even when they were prepared successfully, they did not have adequate physical properties. Table 4 shows data for the thalious salts which were successfully prepared and which showed good physical properties.

**TABLE 4**  
LONG SPACINGS AND MELTING POINTS FOR SOME THALLIUM SALTS  
OF n-FATTY ACIDS

Compound	Long Spacing, Å	M. P., °C
Tl-C <sub>10</sub>	29.92	46°
Tl-C <sub>12</sub>	30.54	126°
Tl-C <sub>16</sub>	39.22	100°
Tl-C <sub>18</sub>	40.75	112°

A plot of long spacing data for thalious compounds does not result in a straight line as in other metal salts of aliphatic acids, indicating either polymorphic tendencies or abrupt changes in mode of crystallization from member to member in the series.

Many other metal salts or soaps were prepared, some of which were very satisfactory. Sodium, potassium, lithium and calcium form high melting compounds which give strong long spacing reflections. However, as would be expected these compounds were soap-like; softening before melting and difficult to crystallize as single crystals.

Some salts were prepared which appear to be useless for dispersing crystals. Among these are salts of iron, cobalt, nickel, and magnesium which either hydrate badly or form an amorphous glass. Bismuth and manganese form salts which have high melting points but which do not crystallize or order to a great degree. Silver salts probably should be of use and long spacings for a complete set of compounds may be found in a paper concerning the identification of aliphatic acids by the formation of silver salts (ref 9).

A summary of long spacing data is shown in figure 2 for Pb, Cu, and Zn salts of  $C_6$  to  $C_{10}$  acids along with spacings observed from the acids themselves. Spacings for the normally liquid acids were obtained at low temperatures and detailed results on acids from  $C_1$  to  $C_{14}$  may be found in a paper by one of the authors (ref 1). Also shown are spacings from Ca, K, Na, Li, Tl, and  $UO_2$  salts of hexanoic acid ( $C_6$ ). Since the slopes of the lines are about the same, once one or two compounds are prepared, spacings for other members of the series may be roughly predicted.

### Producing Crystals

Thus far only salts of aliphatic acids have been discussed. These salts have the distinct advantage that almost any spacing may be obtained by using the correct acid and metal combination. However, they have the serious disadvantage that single crystals of these salts are quite difficult to grow, at least in a size sufficient for use as a dispersing crystal. There appear to be two possibilities for using these crystals. One is to grow the salts out of solution using the right combination of temperature and solvent to induce the thin, plate-like crystals to grow along the (001) direction on a suitable substrate which could even be bent if necessary to produce an analyzing crystal. The second possibility and one which shows considerable promise (refs 3 and 8) is to use the Blodgett-Langmuir method of building up a crystal one molecular layer at a time from a dipping trough where an acid salt has been allowed to form in a mono-molecular layer. Building such a crystal is time consuming, but results in crystals of high quality. Measurements indicate greater crystal perfection (from rocking curve) in synthetic "crystal gratings" than in some single crystals of comparable spacings.

To show the application of such layered analyzers, figures 3 through 6 were prepared showing spectra obtained by direct excitation with equipment described in reference 3. The dispersing device used was a 42-cycle barium stearate film deposited on a glass microscope slide. In figure 3 the aluminum K lines are shown using direct excitation from Aluminum sheet. The detector for this trace and others in this series was a flow proportional counter with a 0.00015 inch mylar window and operated at reduced pressure and a flow of argon-methane (P-10). As can be seen, the counting rate for  $AlK_{\alpha}$  is quite high, but the peak to background ratio is very poor. Figure 4 shows  $CuL_{\alpha}$  and  $ZnL_{\alpha}$  from brass and gives some idea of the resolution of this dispersing element with a routine fast scan. Figures 5 and 6 show L spectra of nickel and iron, respectively. As can be seen, the efficiency of the counter has dropped off considerably and the count rate is very low in the  $FeL$  or 18 Å region. A thinner window or perhaps a different type detector must be used for longer wavelengths.

Aromatic Acid Salts

Thus far, only salts of phthalic acid have been evaluated. Table 5 shows C parameters for Na, K, Rb, Cs, and Tl salts of phthalic acid (ref 11). The crystal structure of K, Rb, Cs, and Tl salts permits recording of the intense (001) reflection, but unfortunately  $l = 2n$  for the sodium salt. These crystal spacings should permit dispersion of K spectra to oxygen ( $OK = 23.57 \text{ \AA}$ ) and L spectra to vanadium ( $Va L = 24.31 \text{ \AA}$ ). However, spectrometer geometry may not allow scanning to sufficiently high angles to observe these lines.

TABLE 5  
C<sub>0</sub> FOR SALTS OF PHTHALIC ACID

Salt	C <sub>0</sub> , Å	Melting Point, °C
Na	26.42	370
K	13.26	370
Rb	12.99	283
Cs	12.84	290
Tl	12.95	187

These compounds tend to crystallize beautifully and most grow in platelets parallel to the (001) and thus have a natural cleavage in the desired direction for use as an analyzing crystal. Some crystals as large as one inch in diameter have been grown. Reflected intensities are very good but crystal perfection is not always as good as might be desired. However, probably more sophisticated crystal growing techniques could improve the perfection of these crystals.

Figure 7 shows AlK lines from Aluminum sheet using a potassium acid phthalate (KAP) crystal. The peak intensity is comparable to that seen in figure 3 where a layered analyzer was used, but the KAP gives a greatly improved peak to background ratio. However, since measurements were not made at the same angles, Lorentz and polarization factors along with general scatter must be taken into consideration if a direct comparison is desired. Figures 7, 8, and 9 show traces of CuL, NiL and FeL respectively. From all work performed thus far, KAP appears to be a very useful analyzing crystal for the region 5 to 20 Å. Other crystals in this series shown in table 5 have been obtained and are being evaluated.

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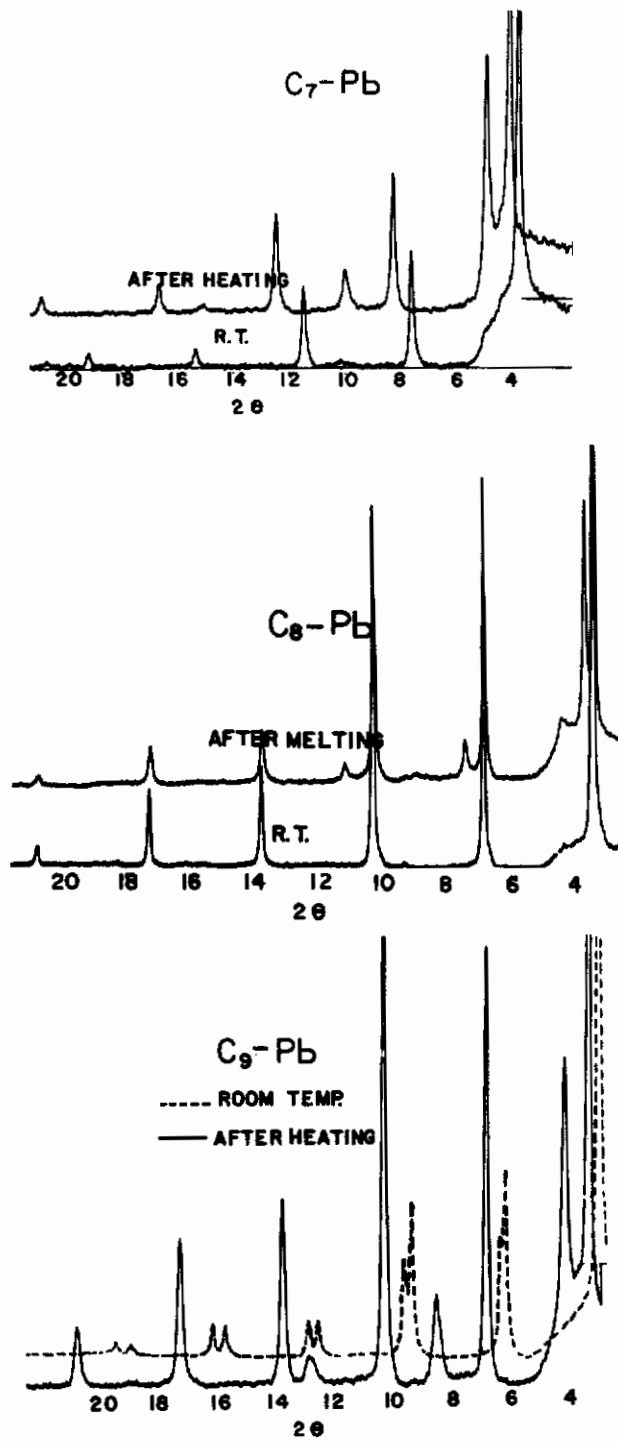


Figure 1. Polymorphic Tendencies in Lead Salts of Carboxylic Acids

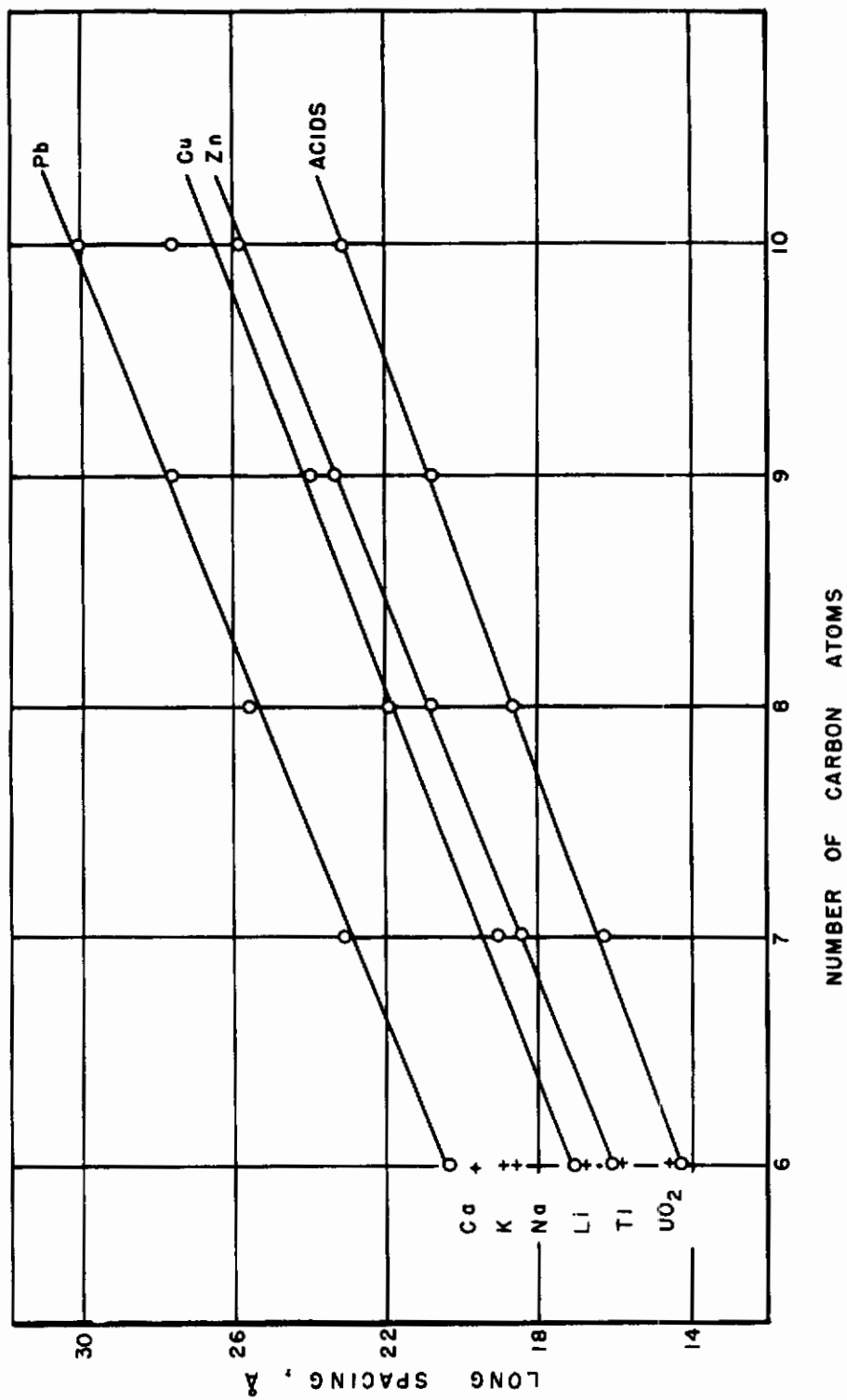


Figure 2. Long Spacing Relationships in Fatty Acids and Metallic Salts of Fatty Acids



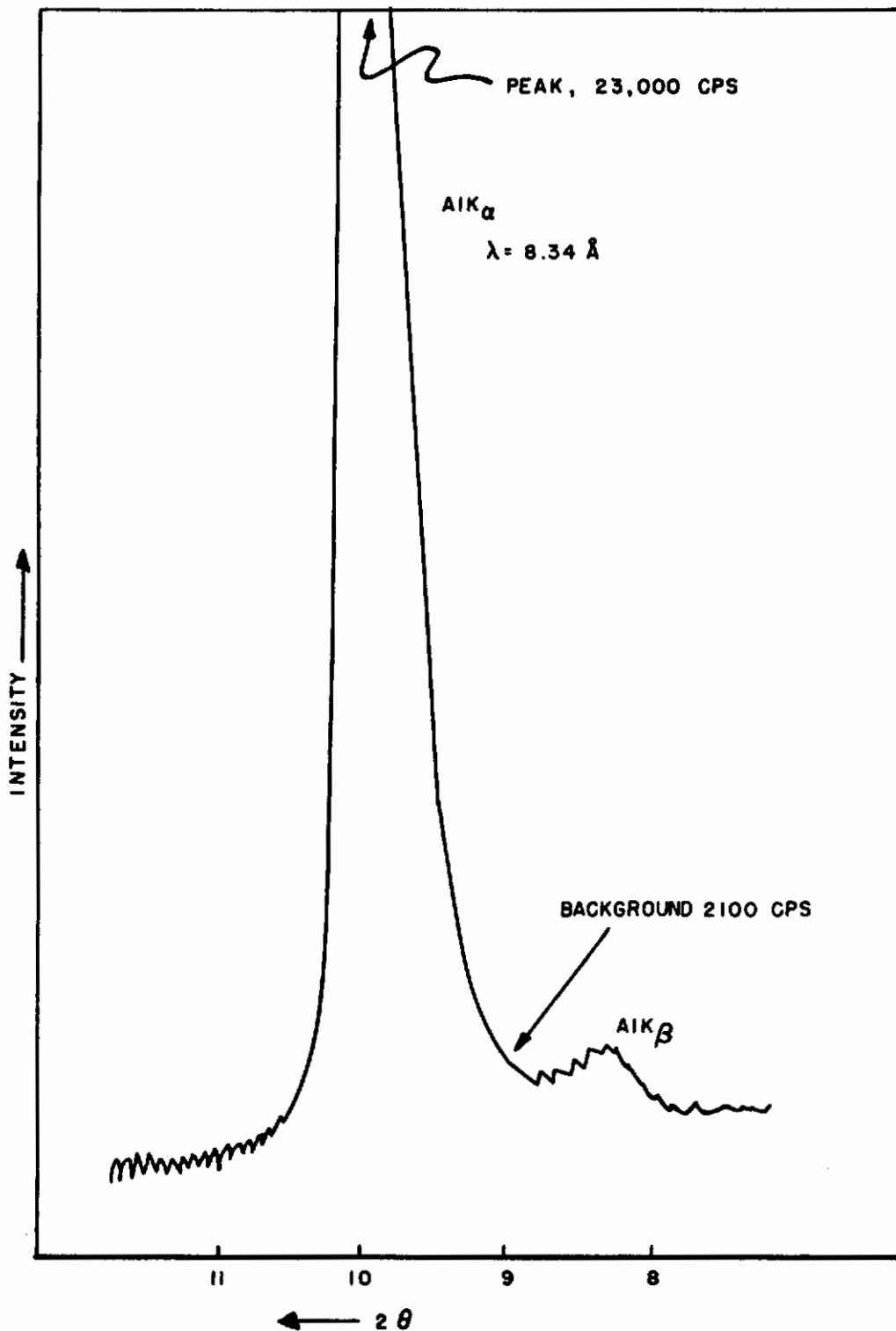


Figure 3. Aluminum K Lines Using 42 Layers of Barium Stearate as Analyzing Crystal (pure Aluminum sheet, 14KV, 1 Ma using flow proportional counter).

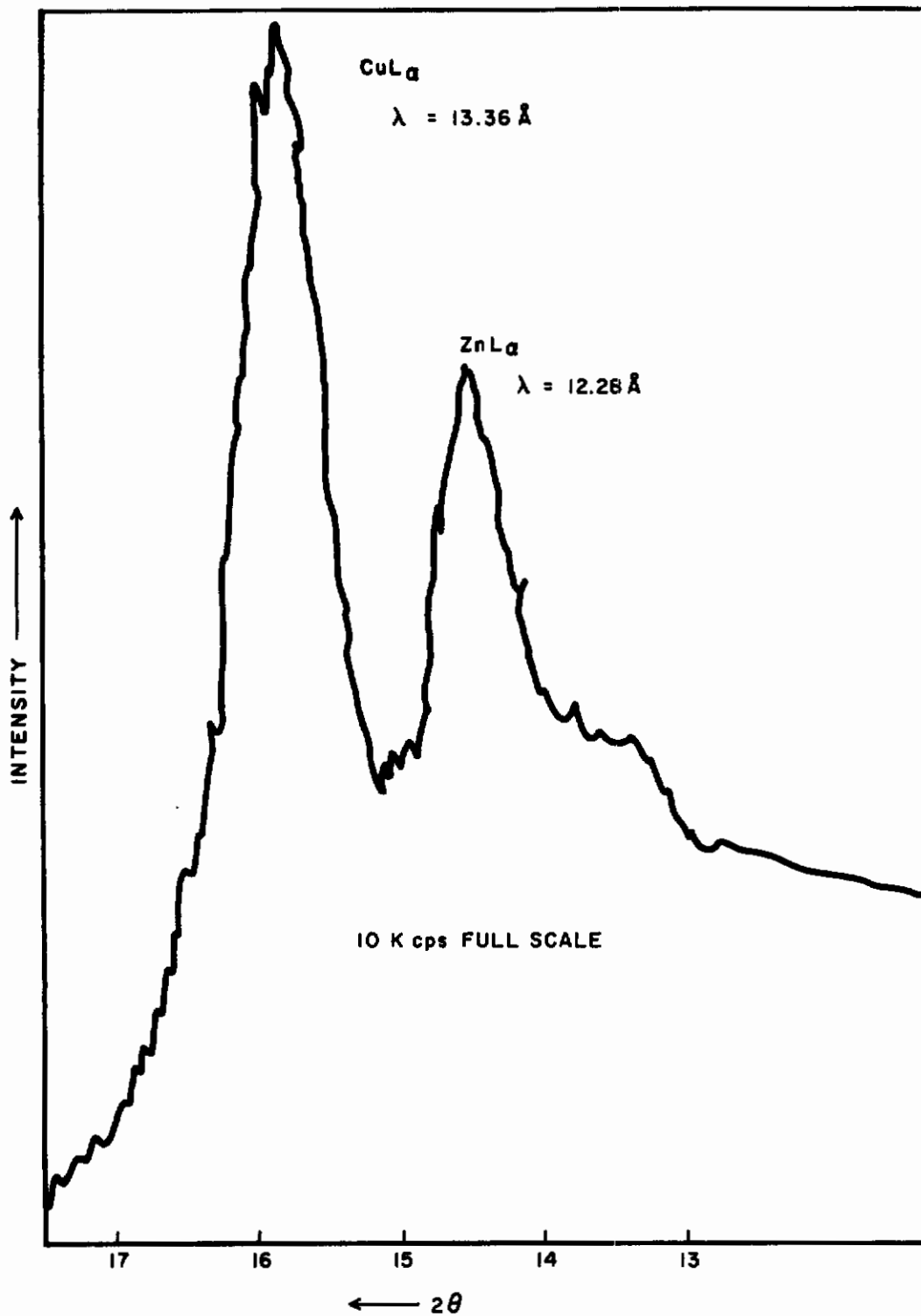


Figure 4. Zinc and Copper L Lines from Brass Using 42 Layer Barium Stearate Analyzer (excitation conditions same as fig. 3).

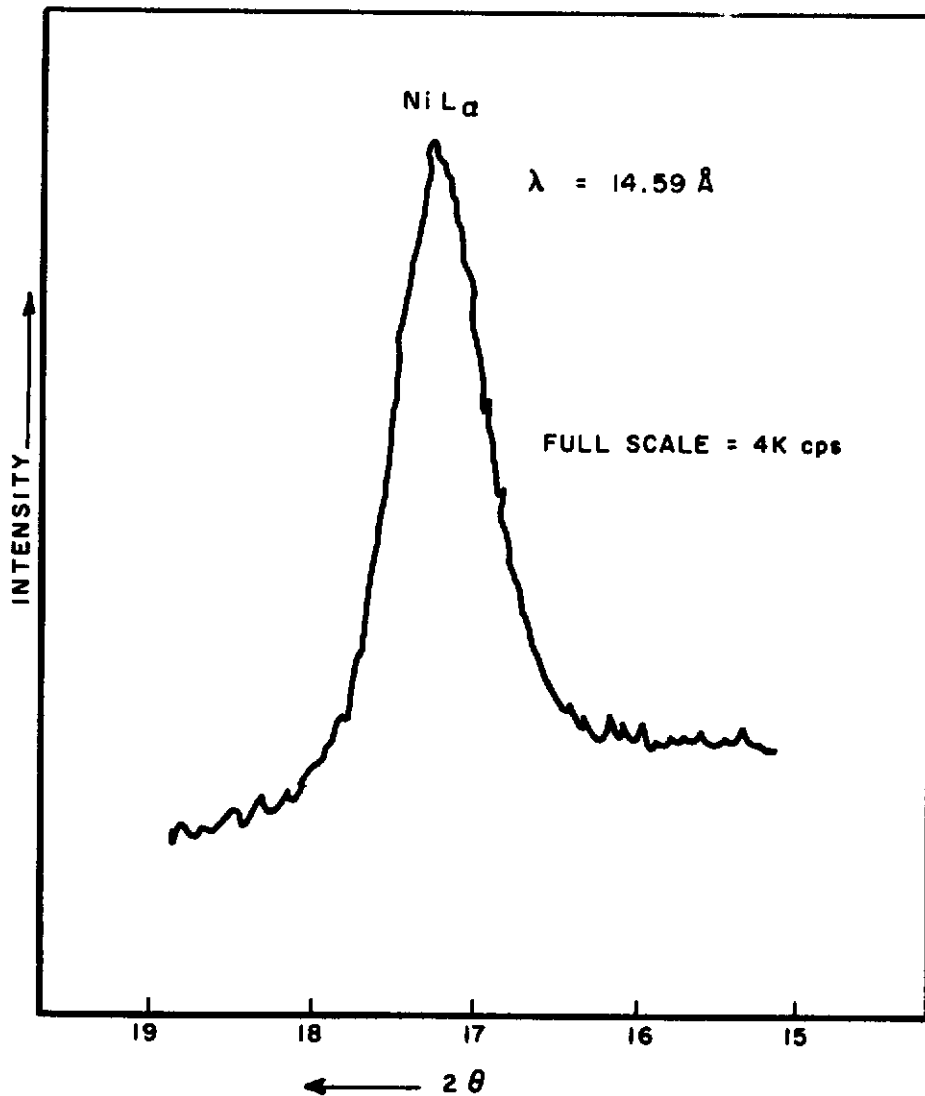


Figure 5. Nickel L $\alpha$  from Nickel Sheet Using 42 Layer Barium Stearate Analyzer (same excitation conditions as figures 3 and 4).

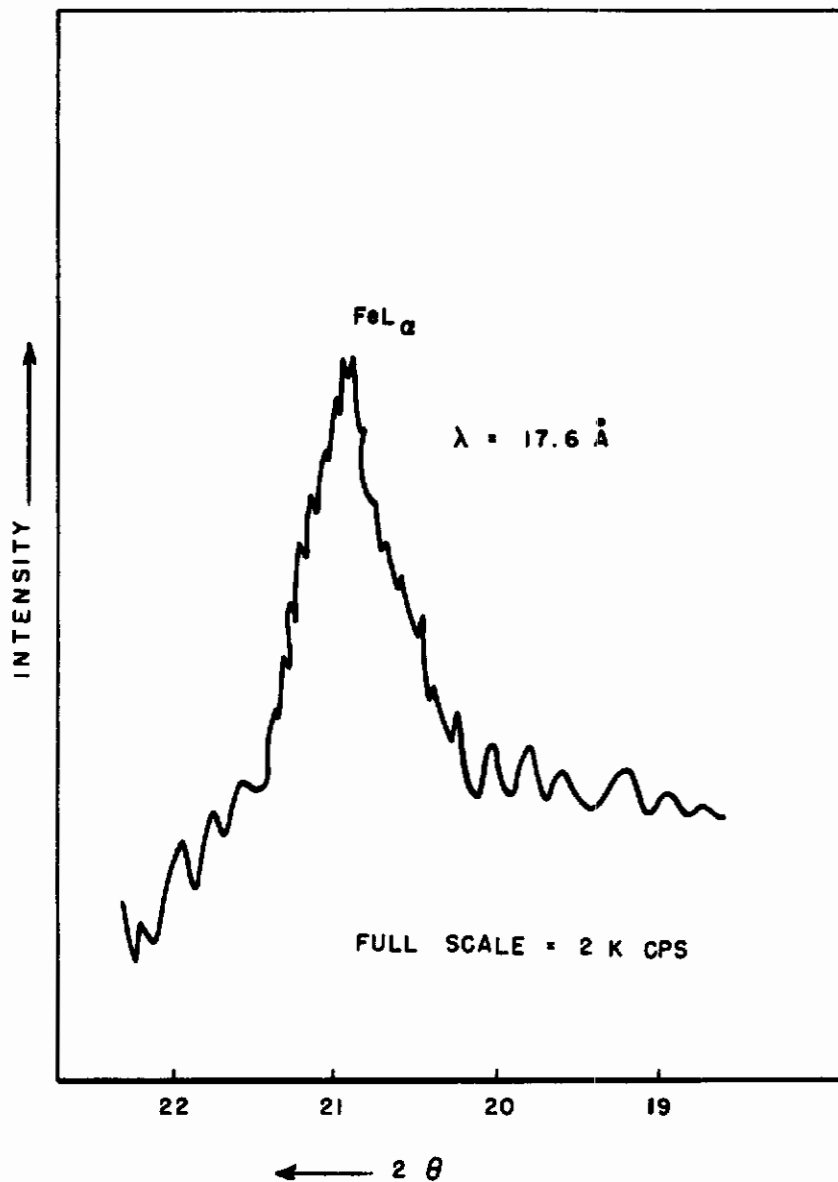


Figure 6. Iron L<sub>α</sub> from Iron Sheet Using 42 Layer Barium Stearate Analyzer (same excitation conditions as figures 3, 4 and 5).

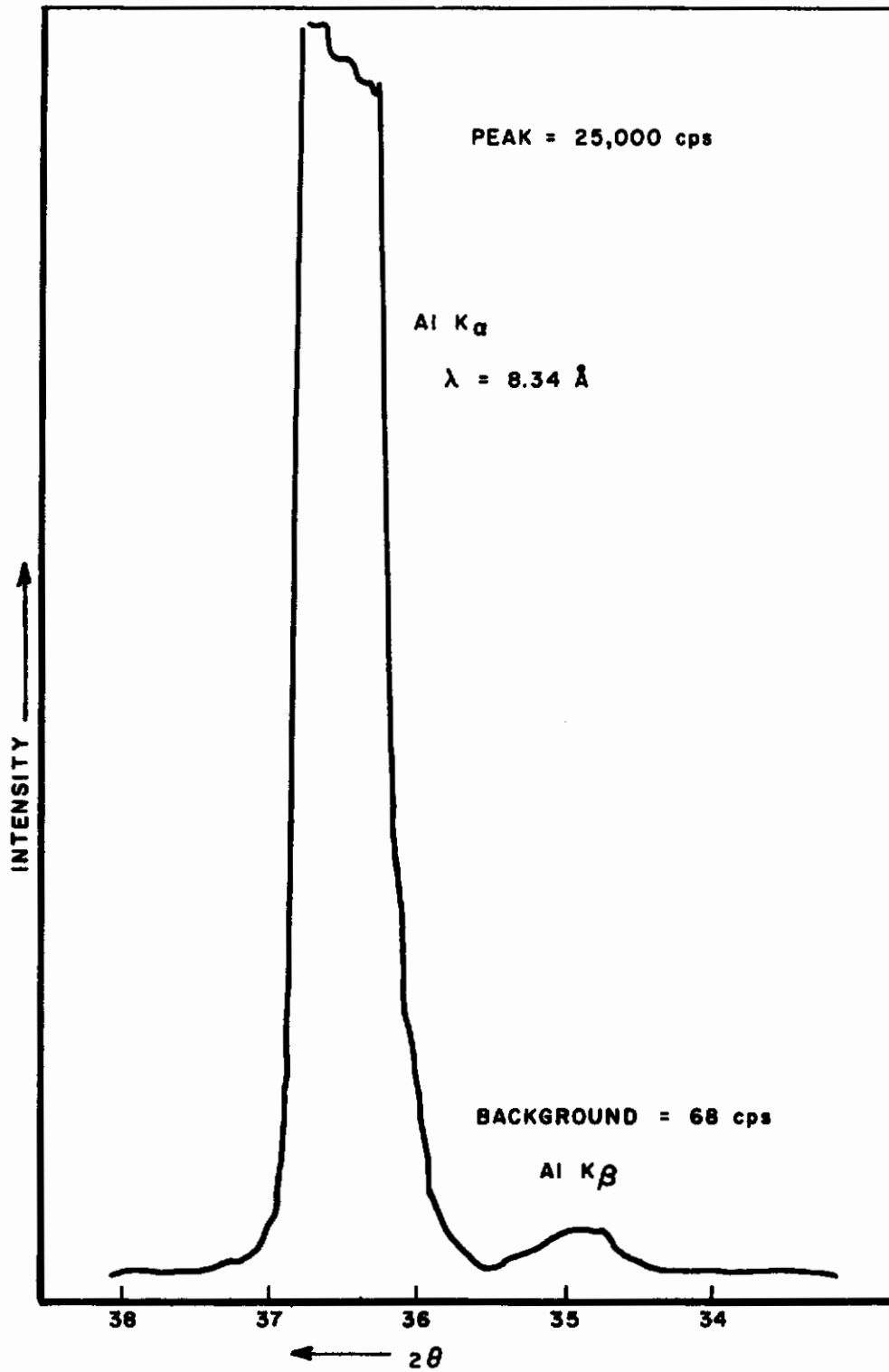


Figure 7. Aluminum K Lines Using Potassium Acid Phthalate as Analyzing Crystal (same excitation conditions as figures 3, 4, 5 and 6).

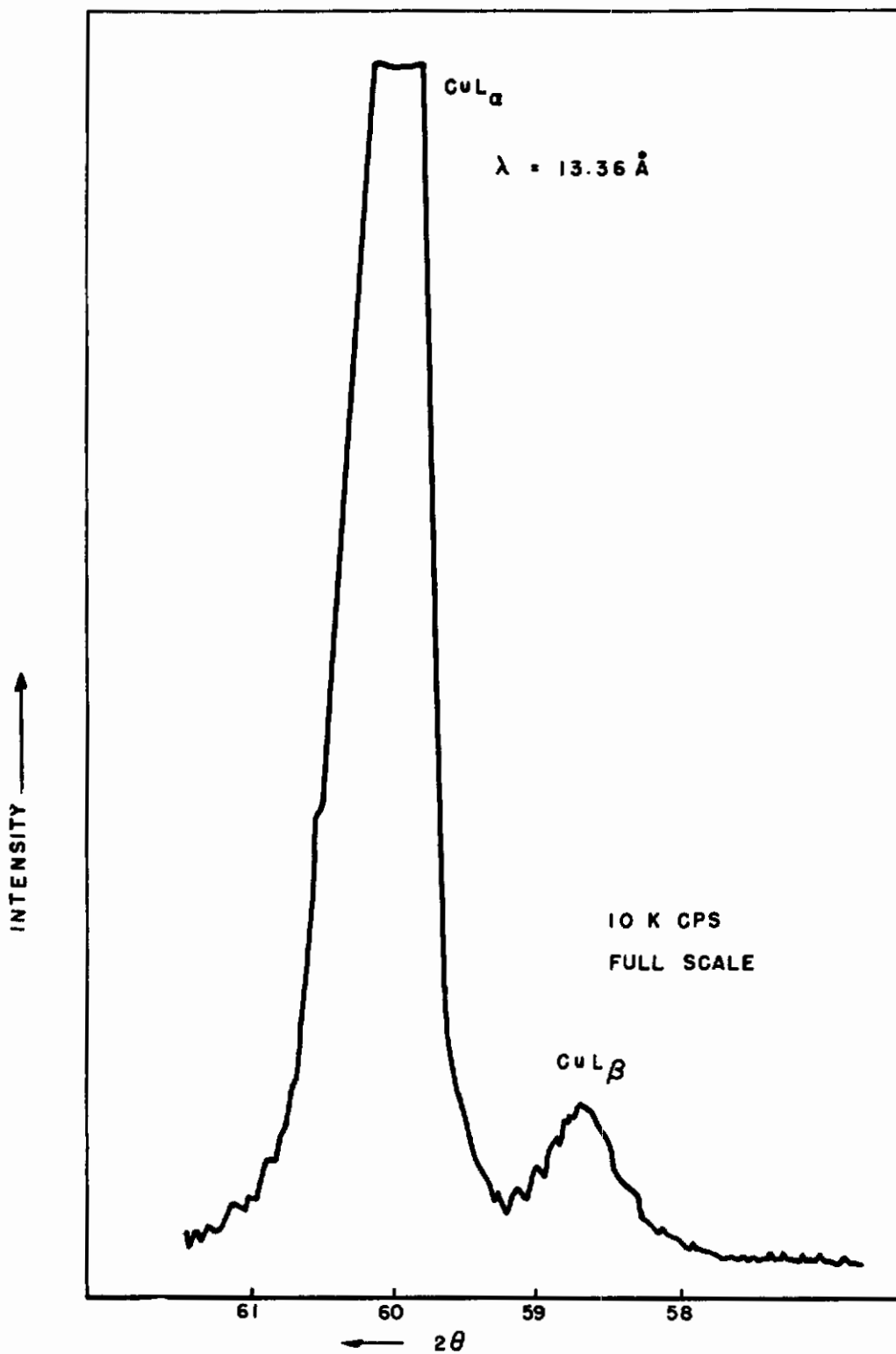


Figure 8. Copper L Lines Using Potassium Acid Phthalate Crystal Analyzer (same excitation conditions as figures 3, 4, 5, 6 and 7).

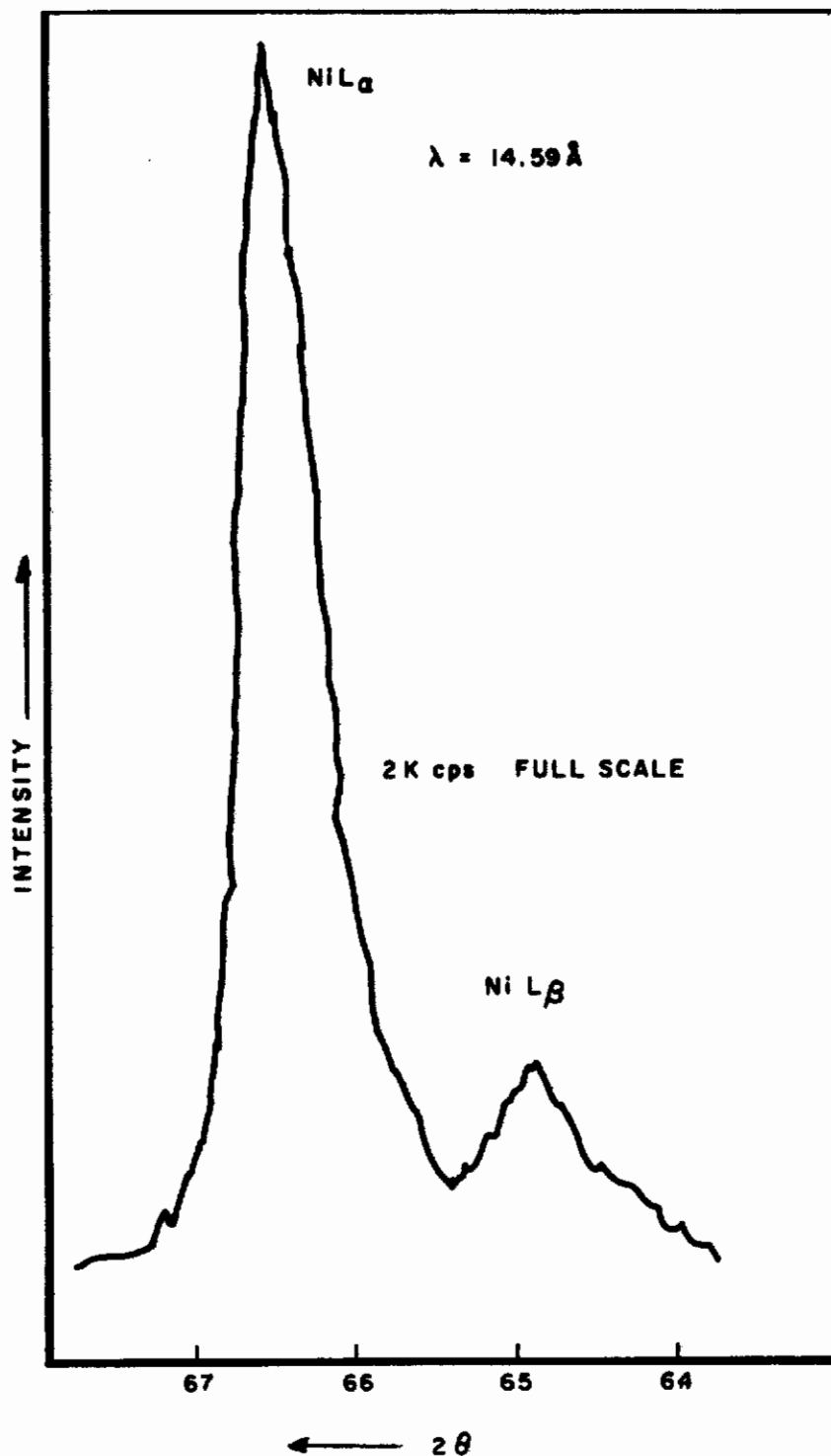


Figure 9. Nickel L Lines Using Potassium Acid Phthalate Crystal Analyzer (same excitation conditions as figures 3, 4, 5, 6, 7 and 8).

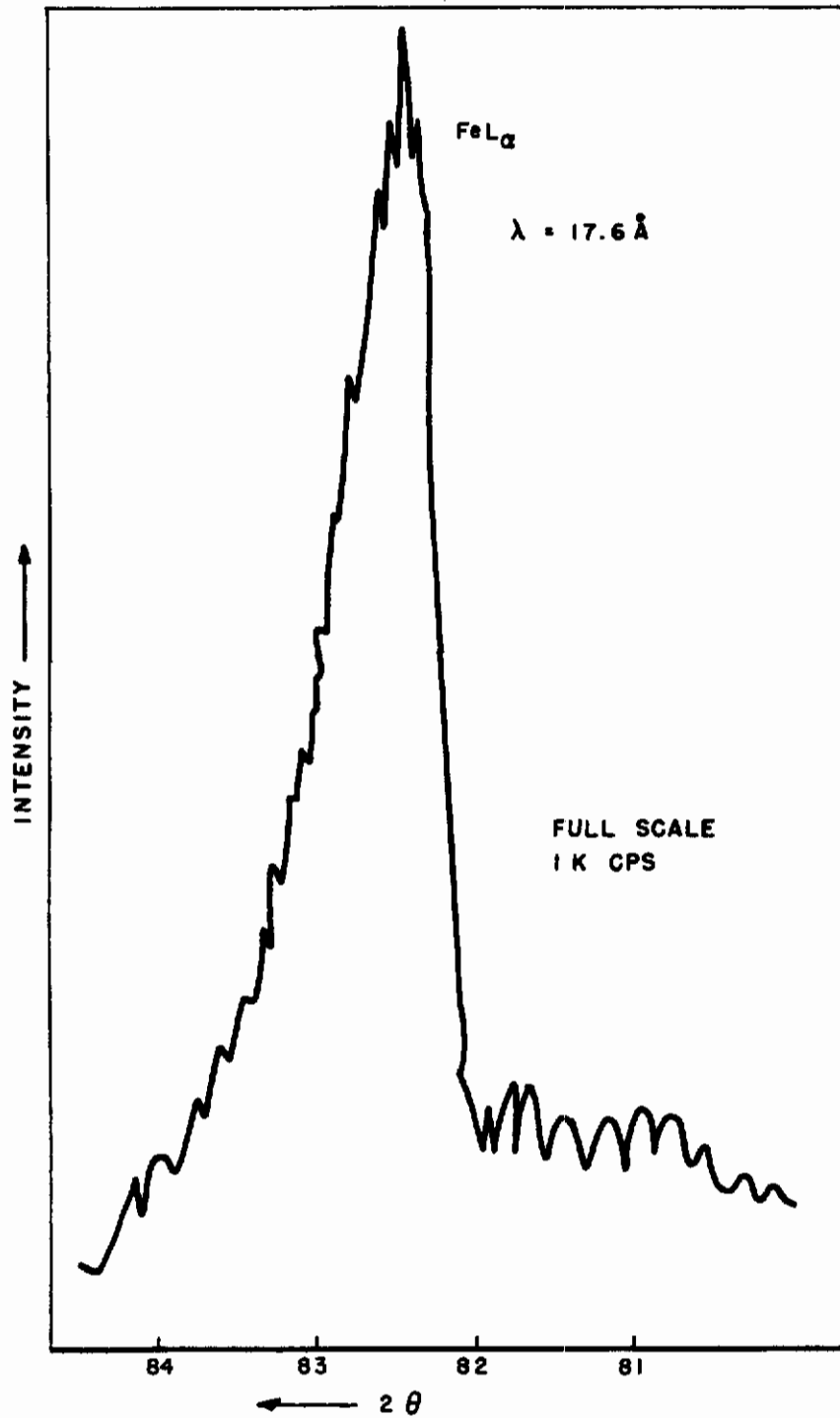


Figure 10. Iron  $L_{\alpha}$  Line Using Potassium Acid Phthalate Crystal Analyzer (same excitation conditions as figures 3 through 9).