

Summer 1975

STUDIES ON COPPER CHALCOGENIDE
HALIDES PART ONE: SYNTHESIS OF
COPPER CHALCOGENIDE HALIDES PART
TWO: THE CRYSTAL STRUCTURE OF
COPPER-BROMIDE-TELLURIDE

PHILIP M. CARKNER

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STUDIES ON COPPER CHALCOGENIDE HALIDES

PART ONE

SYNTHESIS OF COPPER CHALCOGENIDE HALIDES

PART TWO

THE CRYSTAL STRUCTURE OF COPPER BROMIDE

TELLURIDE

by

PHILIP M. CARKNER

B.A., State University of New York at Potsdam

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Department of Chemistry

August, 1975

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TO GINNY

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ABSTRACT

PART ONE

SYNTHESIS OF COPPER CHALCOGENIDE HALIDES

by

PHILIP M. CARKNER

Five chalcogenide halides of copper have been prepared via chemical transport in a temperature gradient. CuClTe , CuBrTe , CuITe , CuClSe_2 , and CuBrSe_3 were synthesized by reaction of the powdered copper(I) halide with selenium or tellurium at various temperatures. The single crystalline product was formed at the lower end of the temperature gradient. The compounds were identified by their previously reported powder diffraction patterns. This method is experimentally less complicated than the hydrothermal technique by which they were originally synthesized.

PART TWO
THE CRYSTAL STRUCTURE OF COPPER BROMIDE
TELLURIDE

by

PHILIP M. CARKNER

Previously reported preliminary crystallographic data for copper bromide telluride has been confirmed in this laboratory. CuBrTe crystallizes in the tetragonal space group $I4_1/amd$ with $a=16.417$ and $c=4.711$ Å. The structure was determined using three dimensional diffraction data gathered on an equi-inclination single crystal diffractometer about the c-axis. Intensities were measured with a scintillation counter. Initial refinement was carried out with block diagonal least squares methods. Subsequent full matrix least squares refinement gave a final conventional R-factor of 0.066. The structure consists of infinite spirals of tellurium atoms parallel to the c-axis. The bromine atoms form tetrahedra which are interspersed between the tellurium spirals. The copper atoms were found to be disordered, partially occupying four sets of special positions. These positions form two basic types, one located in the bromine tetrahedra and the other in a distorted tetrahedral environment with two bromine and two tellurium atoms as nearest neighbors. The Te-Te distance in the spiral is $2.751(3)$ Å and the distance of closest approach of the tellurium spirals is 4.69 Å. The Br-Br

distance in the bromine tetrahedra is $3.933(8) \text{ \AA}$. The various Cu-Br distances vary from 2.241 to 2.659 \AA . The observed disorder could be an explanation for the previously observed semiconducting nature of the compound. This model appears to be the best one, given the available data. Further investigation of the possibility of the presence of a superlattice or polytypes for compounds of this type is indicated.

PART ONE

SYNTHESIS OF COPPER CHALCOGENIDE HALIDES

PART ONE

I. INTRODUCTION

A. Rabenau, H. Rau, and G. Rosenstein have synthesized metal chalcogenide halides of gold¹, copper², antimony, mercury, and bismuth³ via hydrothermal synthesis. The technique used was the same for all compounds with slight variations in parameters. The experimental method used is described in detail elsewhere⁴. A brief outline of the hydrothermal method used by Rabenau will be given here since it was one of our objectives to obtain single crystals of the copper compounds by a simpler method, and it will be useful for comparative purposes.

The reactants (the elements or binary compounds containing the desired elements) are placed in a silica ampoule which is filled with the appropriate 10 molar hydrogen halide acid. The ampoule is then placed in liquid nitrogen to freeze the acid, evacuated, and sealed off. The ampoule is transferred from the liquid nitrogen and placed immediately under hot running water until a film of liquid acid is formed on the inner wall of the ampoule. This is done to prevent bursting of the ampoule due to increase in volume of the melting acid (the reader is cautioned that a heavy face shield should be worn during this operation). The ampoule is kept in a hood until the acid is completely liquid.

The ampoule containing the reactant mixture is placed in an autoclave. Since high pressures are generated during the reaction and there is free space around the

ampoule in the autoclave cavity, solid carbon dioxide is placed in the cavity in order to generate a counter pressure on the outside of the silica tube and to prevent explosion. Internal pressures are not known in most cases so a very high external pressure is applied (again, the reader is cautioned to wear a heavy face shield during these manipulations).

The autoclave is mounted in a two zone tube furnace inclined about 15° to the horizontal to cause convection when a temperature gradient is applied. The autoclave is subjected to the temperatures for the time necessary for the compound being synthesized. The autoclave is cooled and the carbon dioxide allowed to escape from around the reaction tube slowly. After cooling with liquid nitrogen the ampoule is rolled in several layers of filter paper and opened by tapping with a hammer. The contents are transferred to a porcelain dish, washed, and dried. The crystals of the respective compound are isolated mechanically from any accompanying material, e.g., silica chips or other solid phases.

Of the group IB metals only compounds of copper and gold were able to be synthesized. The corresponding silver compounds do not seem to exist. Table I lists the copper and gold compounds reported by Rabenau, et al.. It was also noted that only a formal resemblance seemed to exist between analogous copper and gold compounds. For example, most of the gold compounds exhibit metallic conductivity while the copper compounds are semiconducting. Also the AuBrTe and AuClTe could not be prepared, AuITe was made

Table I

Copper and Gold Compounds Known^a

<u>Copper</u>	<u>Gold</u>
<u>CuClTe</u>	b
<u>CuBrTe</u>	b
<u>CuITe</u>	AuITe
CuClTe ₂	AuClTe ₂
CuBrTe ₂	AuBrTe ₂
CuITe ₂	AuITe ₂
<u>CuClSe₂</u>	AuBrSe
<u>CuBrSe₃</u>	-
CuISe ₃	-

^a Compounds prepared in this work are underlined.

^b The corresponding AuClTe and AuBrTe have not been reported.

along with all three analogous copper compounds.

It was felt that structure determinations would help to explain the apparent anomalous existence of the compounds and the properties of those that were found to exist.

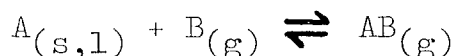
The ultimate aim of this research was structural investigations on some of the copper compounds. In order to do this it was necessary to synthesize single crystals of them. To avoid the expense of a hydrothermal reaction setup we decided to attempt the syntheses via some other method. Rabenau, et al. had reported that the compounds could be made in polycrystalline form by annealing the reactants in a sealed tube. It seemed likely from this information that single crystals could be grown via chemical transport in a temperature gradient.

It was our original intent in the work reported in this thesis to synthesize the compounds by reacting the solid metal halides and selenium or tellurium in a temperature gradient in the presence of the appropriate halogen gas. Solid state reactions carried out in this way are stimulated or promoted by the presence of the gaseous substance. Harold Schäfer⁵ has termed this general process "chemical transport".

It may be argued that the reactions carried out here were not, strictly speaking, chemical transport. The reason for this is that we were able to obtain the desired products without including a specific transporting agent. It is the contention of the author that the reactions to be reported can still be considered to be chemical

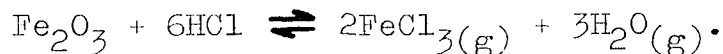
transport. For this reason, along with the fact that work of this type has not been done here before, it is felt worthwhile to include some background on the method of chemical transport.

The term chemical transport reaction as defined by Schäfer⁵ refers to a reaction in which a solid or liquid substance A reacts with a gas to form exclusively vapor phase reaction products, which, in turn undergo the reverse reaction at a different place in the system (having a different temperature or pressure) resulting in the reformation of A.



At first glance this process appears to be related to sublimation or distillation. The distinguishing feature is that the reactant A does not have an appreciable vapor pressure at the temperature involved and is transported or moved chemically rather than physically.

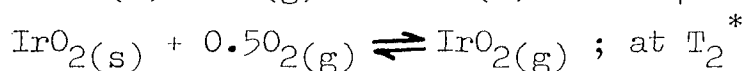
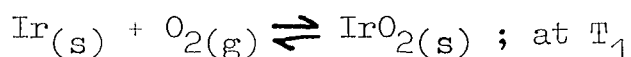
Pure transport processes as defined above have been known for a long time. As early as 1852 Bunsen⁶ observed that the hydrogen chloride in volcanic gases caused Fe_2O_3 to migrate, the controlling feature being the reversible reaction:



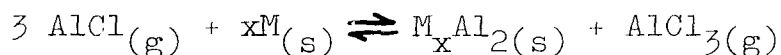
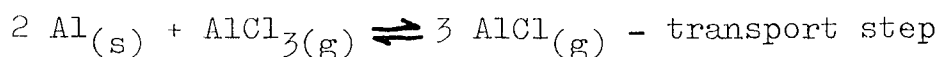
Chemical transport has been used for such purposes as separation and purification of substances, mineralization, preparation of single crystals, and most recently as a synthetic tool. Synthetic schemes usually do not include a pure chemical transport reaction as defined above. Rather

the transport is one of a series of steps or interactions leading to the ultimate product.

There are two cases distinguishable in the role of transport in promoting reactions between solids. (1) The chemical conversion is followed by the removal of the reaction product (by a transport process) in the temperature gradient. This process speeds up the solid-solid reaction by removing the product from the surface of the starting materials, thus preventing the build up of product which often slows down or even stops a reaction. An example of this kind of synthetic use of transport is the synthesis of iridium dioxide.⁷



Iridium dioxide is removed from the surface of the iridium metal via transport as the trioxide and redeposited as IrO_2 . (2) One reaction component in a system in which the starting materials are not in contact reaches the other reactant by means of a chemical transport process. An example of this process is the formation of aluminum alloys⁸,



where M is another metal and the aluminum is transported via its monochloride.

The author's defense of considering the reactions reported in this thesis to be chemical transport will be

* by convention T_2 is always greater than T_1

presented in the results and discussion section. The reactions are thought to be of the first type discussed above.

The applications of chemical transport in synthesis is a relatively new field. The possibilities for use are enormous, and the investigation of mechanisms and identification of the vapor phase intermediates constitute a wide open field for research.

II. EXPERIMENTAL

A. Starting Materials

Reagent grade CuCl_2 (Fisher), C. P. grade CuBr_2 (Fisher), reagent grade KI (Fisher), reagent grade $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Fisher), certified ACS grade $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (Fisher), reagent grade Na_2SO_3 (Fisher), and powdered tellurium and selenium metals (Coleman and Bell) were used in this work without further purification.

B. Preparation of CuCl and CuBr

CuCl and CuBr were prepared by the reduction of the copper(II) halide with sodium sulfite⁹. The freshly prepared CuCl and CuBr were stored in airtight bottles and kept in a desiccator. The identity and purity of the CuCl and CuBr prepared was determined by comparison of their powder diffraction patterns with the pattern reported for the compounds in the Joint Committee on Powder Diffraction Standards (JCPDS) file.

C. Preparation of CuI

CuI was prepared by the reduction of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ by $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in the presence of KI¹⁰. Since CuI retains moisture tenuously the product was dried in vacuo over concentrated sulfuric acid for 3.5 days. The identity and purity of the resultant CuI was also established by comparison of its powder pattern to the one reported in the JCPDS file.

D. The Tube Furnace

The tube furnace used to heat the reaction tubes was a type 70 Electric Multiple Unit Furnace manufactured by Heavy Duty Electric Co.. The furnace has only one temperature zone which can be controlled (as opposed to various multiple zone furnaces which are available for this type of work). The temperature gradient inherent in ordinary tube furnaces of this type is large enough to carry out reactions of the type reported here.

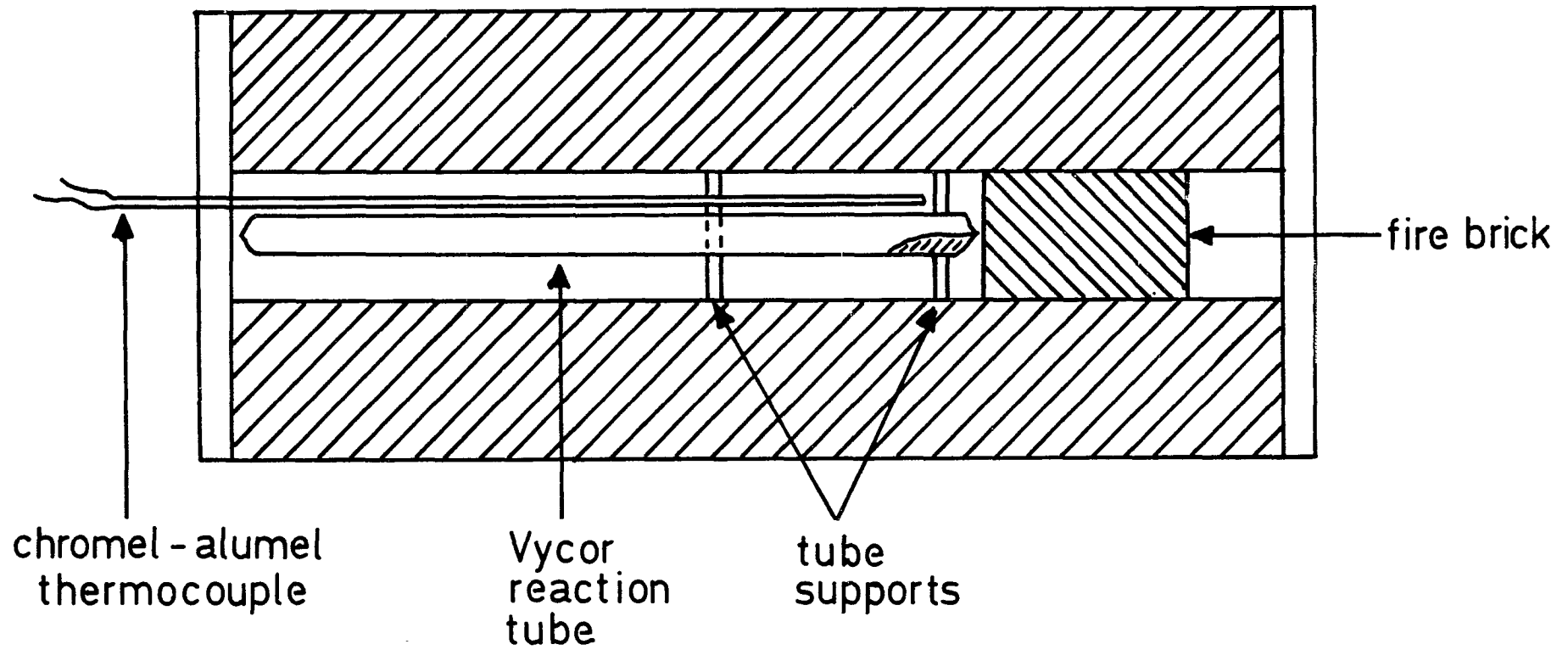
The natural temperature profile of an open ended tube furnace is such that there is a region of constant temperature in the center, decreasing toward both ends. In order to lengthen the region of decreasing temperature the furnace was baffled with fire brick at one side of the center (see Figure 1). This had the effect of forcing the point of highest temperature away from the center, giving a longer temperature gradient in which to place the reaction tube. Temperatures were measured with a movable chromel-alumel thermocouple.

E. X-Ray Powder Diffraction Patterns

All x-ray powder diffraction photographs were taken with nickel filtered copper radiation (wavelength= 1.54178 \AA) in 57.3 mm Philips cameras. The samples were mounted in 0.3 mm glass capillaries. In cases where a powder pattern was desired and only a few crystals were available the samples were prepared by mixing a very small amount of powder with a solution of 20% isoamylacetate and 80% collodion. The mixture was allowed to harden and rolled into a small cyl-

Figure 1

Cross Section of Tube Furnace



inder which was mounted directly in the camera. All films having back reflection lines were corrected for shrinkage and read with a Norelco film reading scale. The intensities were estimated visually for comparison with the data recorded in the JCPDS file.

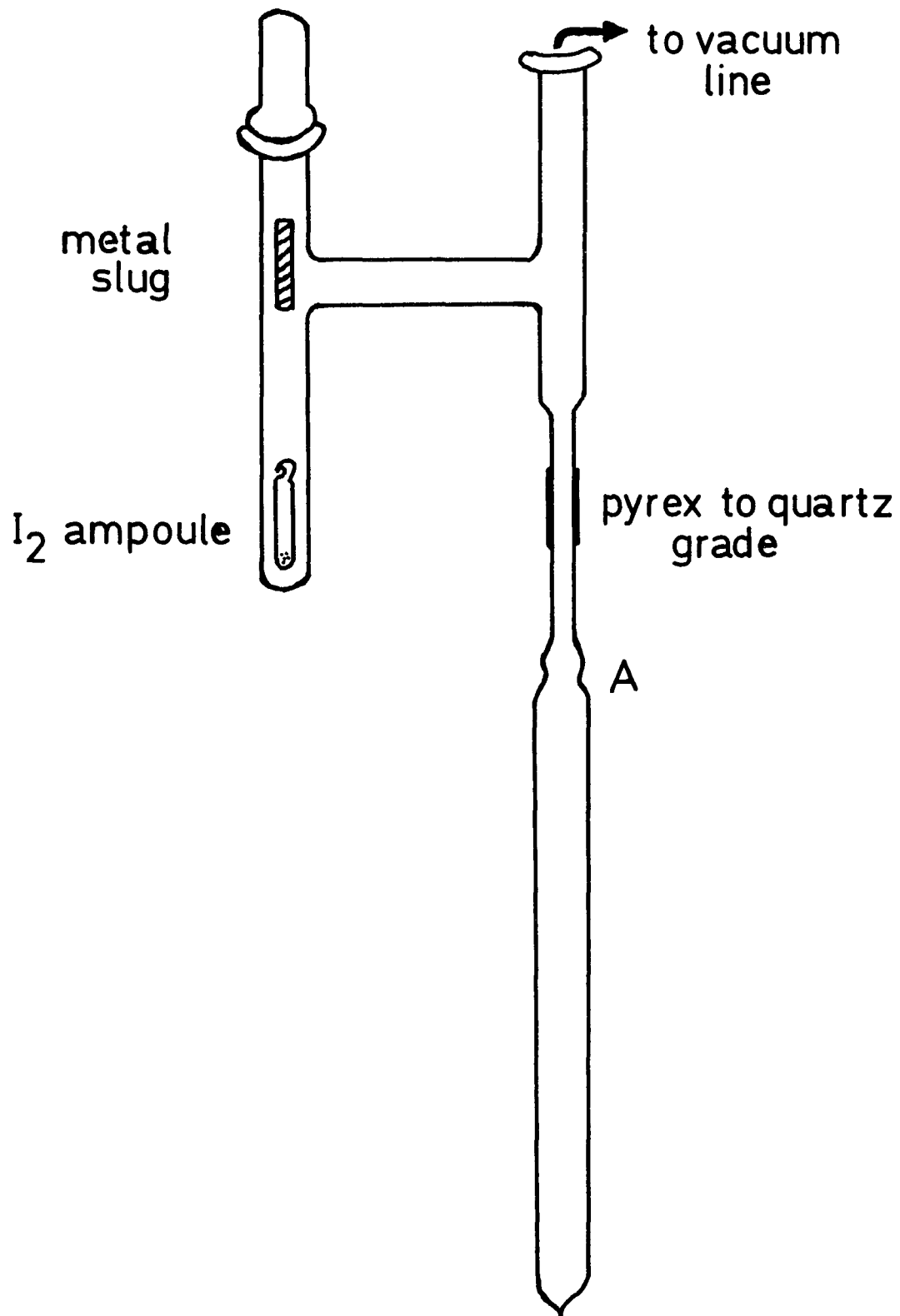
F. Reaction Procedure

The experimental procedure used to synthesize the copper chalcogenide halide compounds was the same in all cases, the only variable being the temperature of reaction. The procedure given here includes the presence of a specific transporting gas. It should be remembered, however, that all the compounds were also synthesized without placing a separate transporting agent in the tube.

The powdered reactants, copper(I) halide and selenium or tellurium, were weighed and mixed physically in a small polyethylene sample bottle. Usually about 1.0g of copper halide and 0.5g of selenium or tellurium were used. Although the exact quantities used does not seem to influence the reaction these quantities gave a convenient volume of material. The mixture of reactants was then placed in a 9 mm x 200 mm Vycor tube which was sealed onto a loading apparatus (figure 2). A small quantity of iodine was then sealed into a small ampoule having a break seal on one end. The ampoule of iodine was then placed in the other arm of the loading apparatus.

The loading apparatus was then connected to a vacuum line and evacuated to 10^{-5} torr for about one hour. After this time the arm containing the reactants was immersed

Figure 2
Loading Apparatus



in liquid nitrogen and the seal on the iodine ampoule broken with a slug of metal. After the iodine was completely sublimed into the reaction tube, the Vycor tube was sealed under vacuum at constriction A, removed from the vacuum line and allowed to warm to room temperature.

The sealed reaction tube was then placed in the tube furnace (figure 1) and heated at the appropriate temperature until small crystals could be observed on the side of the reaction tube. The furnace was then turned off and the reaction tube cooled to room temperature.

Since the reaction tube was sealed under vacuum, care must be taken when it is opened that air does not rush in too fast and blow the crystals about. The tubes were opened in the following manner. The tube was scored around its circumference with a carborundum glass saw at a region where there were no crystals attached to the wall. It was then rolled in a paper towel and snapped open by hand. This method gave a clean break leaving the crystals in their original location and did not shatter the glass, eliminating the tedious task of separating the glass from the crystals manually.

The author has since learned of another method of opening such tubes and would like to mention it here to have recorded it for future reference. Most experimental techniques of this sort are handed down by word of mouth and are difficult to find in the literature. The method is essentially the same as the one used here except that after the tube is scored several layers of masking tape

are wrapped around the point at which the tube is to be broken. A peice of Tygon tubing of the appropriate size also works well. When the tube is snapped the vacuum inside is maintained, and air is then slowly allowed to enter by making a pinhole in the tape or tubing.

III. RESULTS AND DISCUSSION

A. Compounds Obtained

Single crystals of CuClTe , CuBrTe , CuITe , CuClSe_2 , and CuBrSe_3 were obtained using this method. Table II lists the temperatures at which the reactions were carried out. No attempt was made to optimize reaction conditions. The general appearance of the reaction tube after heating is shown in figure 3, the location of product in the tube varying with the compound.

It should be emphasized again that the products were obtained both with a transporting gas (bromine or iodine) and without a specific transporting agent. Ultimately all reactions were run without the transporting gas, as the crystals obtained were purer. The iodine or bromine tended to condense on the surface of the crystals when the tube was cooled.

In all cases the size of the crystals obtained was quite small, varying from a few hundredths to a few tenths of a millimeter. The resultant mixture at the reactant end of the tube always consisted of the product compound along with unused reactants. The powder patterns were the sum of all three of these compounds.

Since the amount of product was very small, no wet chemical analysis was done on the crystals. They were identified by comparison of their x-ray powder patterns to the d-values and intensities originally reported by

Table II

Copper Chalcogenide Halides Synthesized

<u>Compound</u>	<u>Temperature of Reaction ($^{\circ}$C)</u>	<u>Temperature of Product Growth Region</u>	<u>Physical Description</u>
CuClTe	390-420	200	Black prismatic and needle shaped crystals
CuBrTe	420	200	Black prismatic and needle shaped crystals
CuITe	500	300	Black prismatic and needle shaped crystals
CuClSe ₂	300	280	Black prismatic crystals, some needles
CuBrSe ₃	340	290	Dark red prismatic crystals, some needles

Figure 3

Appearance of Reaction Tube After Run



Product crystals
(lower temperature)

Reactant end
(higher
temperature)

Rabenau, et al. which have since been incorporated in the JCPDS file. Since characterization of these compounds is based solely on powder diffraction data, comparison of the stronger d-spacings is given in Tables III-VII. All films gave good clean, sharp lines indicating the compounds were pure. The lines noted as being broad are in areas where the small powder camera did not resolve what would be more than one line from Rabenau's data.

Attempts to synthesize a Cu-Cl-S compound by this method were unsuccessful as were attempts to make the Cu-I-Se compound, although traces of CuISe_3 were observed pure single crystals were not obtained.

B. Comparison of Methods of Synthesis

Five of the copper chalcogenide halide compounds have been synthesized in single crystalline form by two separate methods. The hydrothermal method used originally was outlined briefly in the introductory part of this thesis. If one compares the two methods of synthesis it becomes obvious that the one used here is much simpler and requires less sophisticated and expensive equipment. The other major disadvantage of the hydrothermal method is the high pressures used and the possibility of danger to the experimenter. Also, since the crystals in our method are grown in a region well removed from the reactants, there is no problem of separation of reactant and product after the synthesis, and the process of transport acts as a simultaneous purifying method.

No attempt is being made to belittle the hydrothermal

Table III

X-Ray Powder Diffraction Data for CuClTe

<u>Observed</u>		<u>JCPDS File</u>	
d_{hkl} $\overset{\circ}{\text{A}}$	Intensity ^a	d_{hkl} $\overset{\circ}{\text{A}}$	Intensity ^b
7.57	M	7.82	100
5.43	M	5.52	55
3.94	M	3.95	75
3.49	S	3.49	65
3.19	S	3.21	25
2.95	VS	2.97	65
2.76	MS	2.76	90
2.61	MS	2.62	35
2.16	M	2.17	45
1.946	S	1.953	85
1.797	S	1.796	30
1.567	W	1.561	10

^a S=strong; M=medium; W=weak; V=very

^b Expressed as percent of the strongest line.

Table IV

X-Ray Powder Diffraction Data for CuBrTe

<u>Observed</u>		<u>JCPDS File</u>	
d_{hkl} Å	Intensity	d_{hkl} Å	Intensity
5.73	M	5.81	60
3.56	M	3.57	12
3.27	W	3.27	6
3.00	S	3.04	25
2.89	VS	2.90	100
2.77	W	2.74	18
2.68	M	2.69	16
2.26	M	2.28	25
2.04	VS	2.05	80
1.865	S	1.869	25
1.773	W	1.780	8
1.638	W	1.643	12
1.452	M	1.452	16

Table V

X-Ray Powder Diffraction Data for CuITe

<u>Observed</u>		<u>JCPDS File</u>	
d_{hkl} Å	Intensity	d_{hkl} Å	Intensity
5.96	MS	6.05	18
3.64	M	3.71	18
3.15	S	3.16	30
3.01	S	3.03	100
2.85	M	2.86	20
2.39	W	2.38	14
2.14	M	2.14	35
1.947	M	1.949	20
1.857	W	1.855	10

Table VI

X-Ray Powder Diffraction Data for CuClSe_2

<u>Observed</u>		<u>JCPDS File</u>	
d_{hkl} Å	Intensity	d_{hkl} Å	Intensity
6.83	S	6.94	14
5.16	VS	5.15	100
3.51	S	3.53	10
		3.46	14
3.35	M	3.36	16
2.94	S	2.94	45
		2.92	20
2.78	S	2.78	50
2.67	M	2.67	20
2.58	S	2.57	65
2.25	M	2.25	12
2.13	MS	2.13	25
2.04	M	2.04	10
1.924	MS	1.934	14
1.871	MS	1.871	30
1.822*	S	1.829	18
		1.813	25
		1.809	20
1.729*	S	1.735	25
		1.718	16

* broad

Table VII

X-Ray Powder Diffraction Data for CuBrSe_3

<u>Observed</u>		<u>JCPDS File</u>	
d_{hkl} Å	Intensity	d_{hkl} Å	Intensity
4.44	M	4.48	25
3.75*	S	3.84	18
		3.79	20
		3.73	45
3.34	W	3.38	10
3.00	S	3.01	65
2.91	S	2.91	50
2.85	W	2.86	14
2.67	WM	2.69	25
2.61	S	2.63	100
2.49	W	2.52	14
2.23*	MS	2.26	20
		2.22	14
1.838	M	1.845	50
1.746	WM	1.757	14
1.672*	WM	1.693	14
		1.665	14
1.624	W	1.625	10

* broad

technique for it is a very powerful and versatile method for synthesis and crystal growth¹¹. It is felt, however, that in this specific case the transport method is a superior technique.

C. The Transport Effect

As was mentioned previously, the reactions reported here are thought to involve a legitimate chemical transport process. Since Rabenau² reported that the compounds could be prepared in polycrystalline form by annealing the reactants it is felt that the transport process involved here is of the first type discussed in the introduction. The ternary reaction product is removed from the surface of the reactants and transported chemically to a region of lower temperature where single crystals are formed. The gaseous transporting agent is probably generated in situ. The pungent odor of the halogens could be noticed when the reaction tubes were opened. During the course of heating the reaction tube there was a purple vapor present in the tube during reactions involving CuI and a brown vapor when CuBr was used. Chlorine, bromine and iodine are all very common transporting agents⁵.

D. Suggested Further Work

No specific proposal can be made at this time as to the nature of the gaseous intermediate or other vapor phase species that may be present in these systems.

It seems at this point that investigation of the gas phase atoms or molecules would be extremely enlightening. Spectrophotometric methods should prove to be very

useful for these investigations. Thermodynamic and mechanistic knowledge about transport systems in general is still quite scarce. The process is used mainly as a means to obtain an end (a compound, single crystal, etc.), and its users have been thus far mostly results oriented. Detailed knowledge of the chemistry is known mainly for relatively few simple systems.

The study of chemical transport from a basic point of view is still a wide open field and promises to be a fruitful one.

PART TWO

THE CRYSTAL STRUCTURE OF COPPER BROMIDE
TELLURIDE

PART TWO

I. INTRODUCTION

Metal chalcogenide halides such as the copper compounds dealt with in the first part of this thesis constitute a very novel class of chemical compounds. These ternary compounds vary widely in stoichiometry. For the most part they form a class of inorganic compounds that would not be predicted on the basis of the common oxidation states of the constituent elements.

In particular, interest in the group IB metal compounds was the impetus for this work. The copper and gold compounds known to exist are listed in Table I. The method of synthesis used for the copper and gold compounds has apparently not been successful in preparing the analogous silver compounds. Rueter and Hardel, however, reported Ag_3SBr and Ag_3SI ^{12,13}. Attempts to synthesize copper and gold chalcogenide halides with sulfur as the chalcogenide have also been unsuccessful.

The electrical conductivity of the compounds, studied by Rabenau, et al.³ also offers some points of interest. The AuXTe_2 (X=Cl,Br,I) compounds are metallic conductors. All of the copper compounds are semiconductors. AuITe is also a semiconductor. The analogous AuClTe and AuBrTe could not be prepared. All three copper compounds CuXTe (X=Cl,Br,I) exist.

The irregularities in which compounds exist are not readily explainable nor are the observed conducting properties. It was felt that structural studies on these compounds might suggest explanations for some of these observations.

The crystal structures of AuBrSe¹⁴, AuClTe₂, and AuTe₂¹⁵ have been reported. No obvious explanation was found for the metallic conductivity of AuClTe₂ and AuTe₂.

This work reports the first complete structure determination in the series of copper compounds. The compounds CuClTe, CuBrTe, and CuTe were reported by Rabenau to all belong to the same space group, I4₁/amd. It was felt worthwhile to determine the structure of one of these compounds. If they are isostructural as indicated by their space group, a structural investigation on one would essentially determine the structures of all three.

II. EXPERIMENTAL

A. Preparation of Single Crystals of CuBrTe

Single crystals of CuBrTe were prepared directly by reaction of CuBr and tellurium in a temperature gradient as reported in part one of this thesis.

B. Determination of the Space Group and Unit Cell Dimensions

Preliminary Weissenberg photographs showed tetragonal symmetry with the following systematic absences; $hkl: h+k+l=2n$, $hk0:h,(k)=2n$, $0kl:k+l=2n$, $hhl:(l=2n)2h+l=4n$. These systematic absences indicate the unique space group $I4_1/am\bar{d}$, no. 141 in the International Tables¹⁶.

The unit cell constants were determined from rotation and zero level Weissenberg photographs taken about $[100]$ and $[001]$ with nickel filtered Cu-K α radiation (wavelength=1.54178 Å). Computer programs WEISS and ROTOSC¹⁷ were used to calculate cell constants from film measurements. The unit cell constants and other data pertinent to CuBrTe are given in Table VIII. All measurements were made at 21°C.

The measured density, D_m , is that reported by Rabenau, et al. and corresponds to 16 formula units per unit cell.

C. Crystal Description and Measurement

The crystal used for intensity data collection was mounted with the c-axis parallel to the rotation axis of the goniometer head. The c-axis corresponds to the longer macroscopic crystal dimension. Since the linear absorption coefficient, μ , for CuBrTe is 291.22 cm^{-1} it was considered

Table VIII

Crystal Data for CuBrTe

Tetragonal; $I4_1/amd$

$$a_o = 16.417 \pm 0.246 \text{ \AA}$$

$$b_o = 16.417 \pm 0.246 \text{ \AA}$$

$$c_o = 4.711 \pm 0.071 \text{ \AA}$$

$$\alpha = 90.00 \pm 1.35^\circ$$

$$\beta = 90.00 \pm 1.35^\circ$$

$$\gamma = 90.00 \pm 1.35^\circ$$

$$V = 1269.697 \text{ \AA}^3$$

$$D_m = 5.62 \text{ g.cm}^{-3}$$

$$D_x = 5.674 \text{ g.cm}^{-3}$$

$$Z = 16$$

$$\mu = 281.22 \text{ cm}^{-1}$$

$$F_{000} = 1856$$

worthwhile to make an absorption correction on the intensity data. Any method for correcting intensity data for absorption depends upon calculating the length of the beam path in the crystal for each reflection¹⁸. Therefore it is essential that the crystal faces be measured accurately. The crystal faces are described by equations calculated from these measurements. These equations are used by the computer program in calculating the length of the beam path for each reflection.

The dimensions of the crystal faces were measured with monocular and binocular Leitz microscopes. Both microscopes had internal light sources and contained eyepiece scales. The scales were calibrated by placing a stage micrometer under the lens and determining the number of millimeters corresponding to each eyepiece division for the magnification being used. The magnifications employed were 50 and 100 X.

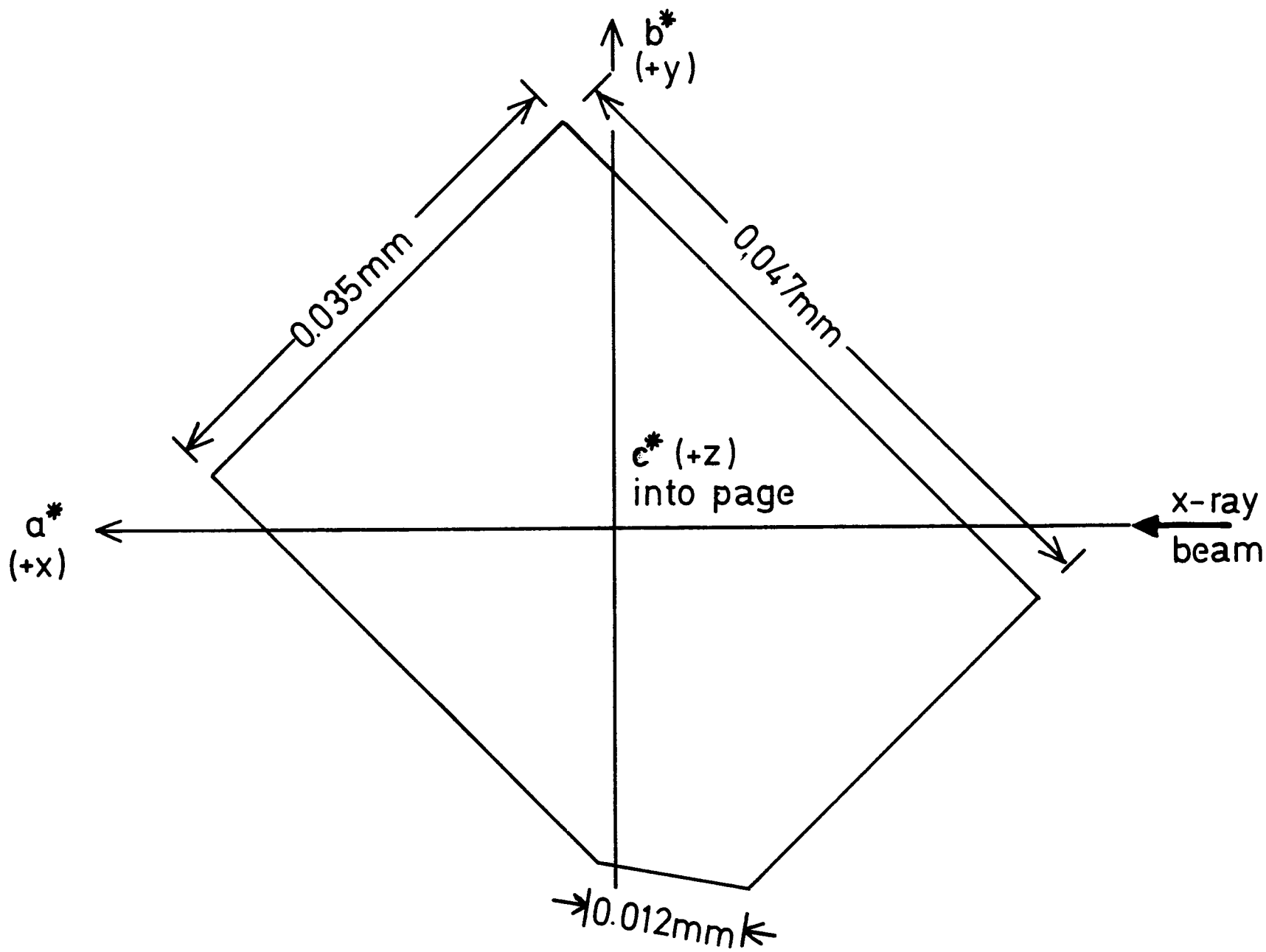
The crystal used to collect intensity data was 0.035 x 0.047 x 0.112 mm. It had five faces parallel to the c-axis and two faces perpendicular to the c-axis. Figure 4 shows a cross section of the crystal used. The crystal is shown oriented such that the crystallographic reciprocal cell axes a^* , b^* , and c^* coincide with the diffractometer axes x, y, and z.

D. Orientation of Crystal on Diffractometer

In order to make an absorption correction, great care must be taken in orienting the single crystal on the

Figure 4

Cross section of CuBrTe crystal
showing the macroscopic orientation
of the crystal faces with respect to
the reciprocal cell axes (a^* , b^* , c^*)
and the diffractometer axes (x , y , z).



diffractometer. It is essential to know the exact physical orientation of the crystal faces as well as the orientation of the reciprocal axes with respect to the x-ray beam (figure 4). The reason for this is that reflections which are theoretically equivalent, i.e., hkl and $\bar{h}\bar{k}\bar{l}$, will show different diffraction intensities due to absorption if the crystal shape is irregular and does not show in its shape the full symmetry of its Laue group¹⁹. Systems of high symmetry offer even more equivalences in reflections. For example in a tetragonal system, the reflections $h00$, $0h0$, $\bar{h}00$, and $0\bar{h}0$ are all equivalent. If care is not taken to ensure that the correct path lengths are being calculated the absorption correction can actually increase rather than decrease the error.

The procedure used here was as follows. A strong reflection was chosen on the indexed Weissenberg film, 800 for example. The azimuth angle (ϕ) for the reflection can be read from the film. When the crystal faces were measured, the goniometer head containing the crystal was supported on the base of the Donnay optical analyzer. This device maintains the same relative orientation of azimuth scale to crystal faces (or goniometer head arcs) as the Weissenberg camera. Knowing the azimuth angles of each crystal face then enables one to know the exact orientation of the crystal with respect to the x-ray beam when a given reflection is in diffracting position.

The crystal is then placed on the diffractometer. When this is done the relative orientation of the azimuth

scale and goniometer head arcs is lost. One must set the counter angle and rotate the crystal about the azimuth axis to locate what was indexed as the 800 reflection. In the tetragonal system, one encounters a reflection every 90° at any specific counter setting. Here one sees 800, 080, $\bar{8}00$, and $0\bar{8}0$. Knowing the orientation of the goniometer head arcs (or the crystal faces) for the 800 reflection as discussed above, one can then be certain which of the four indexed reflections is causing the diffraction maximum. The scale on the diffractometer azimuth is then set to the value calculated for the reflection being used for orientation.

E. Intensity Data Collection

Intensity data for CuBrTe was collected using zirconium filtered Mo-K α radiation (wavelength=0.71069 Å) on a Charles Supper equi-inclination single crystal diffractometer. The x-ray intensities were counted with a Norelco type 85010100 scintillation tube connected to a Norelco electronic circuit panel model 12206/7. The integrated intensities of the reflections were measured by scanning each peak with a Pace-Supper control unit mounted on the diffractometer. This method of peak measurement is known as the ω scan. Two background counts were taken for each reflection, one on either side of the peak. A strong reflection was chosen in each level and counted prior to data collection. These reflections were recounted for reproducibility periodically. This procedure provides a check for instrument drift or malfunctions. Pertinent

instrumental settings are given in Table IX.

One crystal was used for intensity data collection. Layers 0-4 were collected with the crystal mounted on the c-axis. The procedure used to determine the net relative intensity of a peak was to add the two background counts and subtract the total background count from the overall peak count to give the net relative peak intensity.

A one-sigma test was used to determine which reflections gave net intensities which were large enough to be considered observable. This test considers any reflection having a net intensity less than the square root of the total background count (σ) as being unobserved. 294 reflections were counted, 162 of which were considered observed by the above method.

Table IX

Instrumental Settings and Measurement Parameters

Radiation	Mo-K α
Filter	Zr
Background Counting Time	100 sec.
Peak Counting Time	200 sec.
Background Counting Position	1.67 ^o either side of calculated peak position
Scan Rate	1.0 ^o /min.
P.H.A. Baseline ^a	20.5 volts
P.H.A. Window	19.0 volts
Time Constant	2.0
X-Ray Tube Voltage	40 Kv
X-Ray Tube Amperage	15 mA

^a P.H.A. = pulse height analyzer

III. STRUCTURE SOLUTION AND REFINEMENT

The general procedure for determining the structure of compounds by x-ray diffraction is a fairly standard one and an outline of the method may be found in virtually any text on crystallographic methods. The part of a structure determination which keeps such work from being relegated to the hands of technicians is determining the phases of the reflections by proposing a model suitable to begin refinement with. A discussion of the method of structural analysis is given in reference 20. A summary of the crystallographic programs used in this work is given in Table X.

The raw intensity data were corrected for Lorentz and polarization effects.

It is important to note at this point that the electron density expressions given in the International Tables²¹ do not include equivalence relationships for reflections within the same octant of reciprocal space²². In systems of symmetry higher than orthorhombic the unique data is not sufficient to calculate electron density maps if the Fourier summation program is based on these equations. In our system (tetragonal) the reflections hkl and khl are equivalent. Therefore only the intensities of hkl were measured. Before making Fourier summations the "other half" of the octant of data was generated, i.e. khl was assigned the intensity measured for hkl, and both reflections included in the summation.

Table X
 Crystallographic Programs Used In
 Determination of CuBrTe Structure^a

<u>UNH Identification Code</u>	<u>Purpose</u>
UNH-24A	Calculate diffractometer settings
UNH-37	Test for unobserved reflections
UNH-26-B	Lorentz and polarization corrections, assign standard deviations to reflections
UNH-45-A	Absorption correction
UNH-38	Convert UNH-26-B output to NRC-2 format
NRC-2 ^b	Generate lists tape for input to other NRC programs
NRC-4	Generate overall scale and temperature estimates, Wilson statistics
NRC-7	Data manipulation for high symmetry systems
NRC-8	Fourier summation
NRC-10	Block diagonal least squares refinement
UNH-34-A	Convert NRC format to CRXFLS-3 format
ORXFLS-3	Full matrix least squares refinement
NRC-12	Bond distance and angle calculation
NRC-14	Error analysis
NRC-23	Preparation of structure factor table

^a Programs are listed in approximate order of use.

^b NRC-National Research Council of Canada programs

Table XI contains the general and special sets of equivalent positions for space group 141. The second setting of this space group with the origin at the center of symmetry was used in this work.

A three dimensional unsharpened Patterson function was used to locate the tellurium atoms. The special set 16f with $x = 0.13$ gave coordinates which fit the largest peaks of the Patterson map. Patterson functions for space groups of high symmetry such as this one must be treated with caution. Because of the symmetry present, many of the Patterson vectors fall in the same location and what looks to be a very large peak can be the superposition of several smaller ones. Three cycles of block diagonal least squares refinement with an isotropic temperature factor gave an R-value of 0.4894, where $R = \frac{\sum |F_o|}{\sum |F_c|}$. The theoretical value of R for a model with the proper kind and number of atoms placed randomly in the unit cell is 0.83 for a centrosymmetric system. The R-value of 0.48 here was considerably lower than 0.83 so it was considered a worthwhile model to proceed with.

A three dimensional Fourier map generated from the phases calculated with tellurium on 16f indicated that the bromine atoms could be placed on special set 16h with $y=0.38$ and $z=0.58$. Five cycles of block diagonal refinement with tellurium and bromine using isotropic temperature factors gave an R-value of 0.2199.

Another Fourier map calculated with the phases generated with tellurium on 16f $x=0.14$ and bromine on 16h

Table XI

Co-ordinates of Equivalent Positions for
Space Group $I4_1/amd$, Second Origin

Wycoff Notation	Co-ordinates
	$(0,0,0; 1/2,1/2,1/2) +$
32 i	$x,y,z; x,1/2-y,z; 1/4+y,1/4+x,3/4+z; 1/4+y,1/4-x,3/4+z;$ $\bar{x},\bar{y},\bar{z}; \bar{x},1/2+y,\bar{z}; 3/4-y,3/4-x,1/4-z; 3/4-y,3/4+x,1/4-z;$ $\bar{x},y,z; \bar{x},1/2-y,z; 3/4-y,1/4+x,3/4+z; 3/4-y,1/4-x,3/4+z;$ $x,\bar{y},\bar{z}; x,1/2+y,\bar{z}; 1/4+y,3/4-x,1/4-z; 1/4+y,3/4+x,1/4-z.$
16 h	$0,x,z; 0,1/2-x,z; 1/4+x,1/4,3/4+z; 3/4-x,1/4,3/4+z;$ $0,\bar{x},\bar{z}; 0,1/2+x,\bar{z}; 3/4-x,3/4,1/4-z; 1/4+x,3/4,1/4-z.$
16 g	$x,1/4+x,7/8; \bar{x},1/4+x,7/8; x,1/4-x,7/8; \bar{x},1/4-x,7/8;$ $\bar{x},3/4-x,1/8; x,3/4-x,1/8; \bar{x},3/4+x,1/8; x,3/4+x,1/8.$
16 f	$x,0,0; x,1/2,0; 1/4,1/4+x,3/4; 3/4,1/4+x,3/4;$ $\bar{x},0,0; \bar{x},1/2,0; 3/4,3/4-x,1/4; 1/4,3/4-x,1/4.$
8 e	$0,1/4,z; 0,3/4,1/4+z; 0,3/4,\bar{z}; 0,1/4,3/4-z.$
8 d	$0,0,1/2; 0,1/2,1/2; 1/4,1/4,1/4; 1/4,3/4,3/4.$
8 c	$0,0,0; 0,1/2,0; 1/4,1/4,3/4; 1/4,3/4,1/4.$
4 b	$0,1/4,3/8; 0,3/4,5/8.$
4 a	$0,3/4,1/8; 0,1/4,7/8.$

$y=0.38$ and $z=0.62$ gave a set of peaks consistent with special set 16g with $x=0.36$. The copper atoms were assigned this set of positions. Five cycles of block diagonal refinement using isotropic temperature factors gave an R-value of 0.1335.

At this point the data were corrected for absorption, hoping to make the structure factor agreement better. A correction for absorption was applied to the data using a program originally written by J.A. Ibers for equi-inclination Weissenberg geometry. Some minor modifications were made to make the program compatible with the other crystallographic programs at UNH. The absorption correction program was checked for accuracy by a method proposed by Cahen and Ibers²³. 512 points of integration were used. The transmission coefficients, T , in the expression $I_{\text{corr}} = I_{\text{obs}}/T$ ranged from 0.37 to 0.39, a very narrow range.

After four cycles of block diagonal refinement the R-value was 0.1333. Virtually no improvement was found after correcting for absorption. This was not very surprising since the range of transmission coefficients was so small. The only effect observed was a reduction in the overall scale factor.

Next a refinement with anisotropic temperature factors for tellurium and bromine was tried, allowing for the "beta" restrictions imposed by space group symmetry^{24,25} on the anisotropic temperature factors. Three more cycles of refinement gave a small reduction in R to 0.1276.

It was felt that better agreement should be possible.

On the assumption that the locations of tellurium and bromine were probably correct, a difference map was generated using the phases calculated with only tellurium and bromine.

This map also gave a set of peaks at locations consistent with set 16g. There were also a set of smaller peaks with locations consistent with special sets 4a and 4b.

This seemed to indicate that there was more than one kind of copper atom in the structure. Copper atoms were assigned 16g with $x=0.36$ and an occupation factor of 0.5, accounting for eight of the sixteen copper atoms. The remaining eight coppers were assigned the positions 4a and 4b. Five cycles of refinement, again with isotropic temperature factors gave $R=0.1055$. This agreement was better but the isotropic temperature factors for copper on 4a and 4b were extremely high.

At this point the locations of copper and bromine were interchanged. The reason for this being that they are fairly close in number of electrons and their electron density peaks may have been interpreted incorrectly. Bromine was placed on set 16g and copper on set 16h. The resultant R-value was much worse than for the original assignment. The bromine and copper atoms were returned to their original positions.

It was noticed that bromine could be placed on the set 16h with $x=0.38$ or $x=0.11$. To be sure that there were no differences, several cycles of refinement were done with tellurium on 16f with $x=0.14$ and bromine on 16h with $x=0.11$.

Identical results were obtained with an R-value of 0.2175. The x coordinate for bromine was left at 0.11 for the rest of the determination.

Further study of the sets of special positions revealed that if one assigns $z=0.85$ for set 8e, a set of positions are generated such that four pairs of points result. Each one of these pairs has the same x and y coordinate as one of the points from the set 4a and fall on either side of the 4a point in the $\pm z$ direction. In other words, the set 8e with $z=0.85$ generates a set of four pairs of points each centered about a 4a point. A similar situation exists for the set 8e with $z=0.35$ and the set 4b.

Five cycles of block diagonal least squares refinement with:

Te-16f; o.f.* = 1.0
 Br-16h; o.f. = 1.0
 Cu-16g; o.f. = 0.5
 Cu- 8e; o.f. = 0.5 ($z=0.85$)
 Cu- 8e; o.f. = 0.5 ($z=0.35$)

gave an R-value of 0.1017, slightly better than the 4a, 4b assignments. The isotropic temperature factors for the coppers on 8e sets were still high.

Next occupation factors were refined for the copper atoms. An R-value of 0.0940 was obtained for the following occupation factors.

Cu-16g; o.f. = 0.465
 Cu- 8e; o.f. = 0.276
 Cu- 8e; o.f. = 0.295

If one assumes occupation factors of 0.5, 0.25, and

* o.f. = occupation factor

0.25 respectively this would account for twelve of the sixteen copper atoms. A set of peaks with small intensity from the difference map used previously was assigned to copper on 16f with $x=0.36$ and occupation factor 0.25. Refinement of the occupation factor for this set converged at zero. This assignment was abandoned.

The occupation factors for the copper locations 16g, 8e, and 8e were fixed at 0.5, 0.25, and 0.25 respectively and the refinement carried to $R=0.0919$. A difference map was generated from the phases calculated with tellurium on 16f, bromine on 16h, copper on 16g (o.f.=0.5), 8e (o.f.=0.25), and 8e (o.f.=0.25). This map indicated a set of small peaks fitting set 16h with $x=0.32$ and $z=0.14$. These points were thought to account for the four coppers not yet included.

Before including these copper atoms, the coppers originally put on 16g were assigned to the general set 32i with $x=0.36$, $y=0.62$, $z=0.86$, and o.f.=0.25. This has the effect of relieving any possible artificial constraints imposed by the special set 16g without actually moving the atoms in the model.

Refinement was carried out with tellurium on 16f, bromine on 16h, copper on 32i (o.f.=0.25), 8e (o.f.=0.5), and 8e (o.f.=0.5) accounting for sixteen copper atoms. An R factor of 0.1054 was obtained, not quite as good as with 8e occupation factors of 0.5 but the temperature factors were lower.

Refinement was now carried out with tellurium, bromine

(as above), and copper on 32i (o.f.=0.25), 8e (o.f.=0.25), 8e (o.f.=0.25), and 16h (o.f.=0.25). Seven cycles of block diagonal least squares refinement gave an R-value of 0.0795. The temperature factors for the copper atoms were much lower at this point. Nine cycles of block diagonal refinement with anisotropic temperature factors for tellurium and bromine gave an R of 0.0730. Inclusion of anomalous dispersion factors²⁶ had no effect on the agreement.

All attempts to refine with anisotropic copper temperature factors were fruitless, giving very large R factors. The positional and thermal parameters would not converge under these circumstances. All subsequent refinement was done with isotropic temperature factors for the copper atoms.

To this point, all refinement had been carried out using unit weights for the structure factors. Refinement with inclusion of another weighting scheme²⁷ using $\sqrt{w}=1/\sigma_F$ gave poorer agreement. In this scheme,

$$\sigma_F = \sqrt{F^2 + \sigma_I^2} - F$$

$$\sigma_F^2 = \sigma_I / LP$$

$$\sigma_I = (\sigma_I^2 + (pI)^2)^{1/2}$$

where w=weight, p=instrument constant=0.02, LP=Lorentz-polarization factor, I=net diffraction intensity, and $\sigma_I = \sqrt{I}$.

Inclusion of the reflections considered to be unobserved raised the R-value.

Three cycles of full matrix least squares refinement using unit weights and observed reflections lowered the

R-value to 0.0657. This refinement was carried out using anisotropic temperature factors for tellurium and bromine and isotropic temperature factors for the copper atoms. Full matrix refinement was also unsuccessful in refining with anisotropic temperature factors for the copper atoms. Agreement was again better with unit weights.

A final difference map showed some small peaks, the largest of which was $2.8 \text{ e}/\text{\AA}^3$. These peaks are somewhat higher than would be expected for the best possible model. They are dispersed at random, however, and are probably a result of the disorder found for the copper atoms. That is, with the available data and crystallographic methods our best model still does not account exactly for the measured electron density for the real crystalline lattice. These differences are manifested by small peaks and valleys in the difference map. If the model was perfect the difference map would be featureless.

In both block diagonal and full matrix least squares procedures the function minimized was $\left| |F_o| - |F_c| \right|^2$. The atomic scattering factors used were those of Hanson²⁸. Table XII gives a summary of the atom locations determined. Table XIII contains the values of the final refined parameters along with their standard deviations estimated from the least squares refinement (in parentheses). The full matrix least squares refinement was performed with the ORXFLS-3 program of Busing, et al.²⁹. The other computations were made with the National Research Council of Canada Crystallographic Programs³⁰. A summary of the successful stages

of refinement is given in Table XIV. Table XV gives the final observed and calculated structure factors.

Table XII

Atom Locations and Occupancy Factors

Atom	Position Set	Occupancy Factor
Te	16f	1.0
Br	16h	1.0
Cu(1)	32i	0.25
Cu(2)	8e	0.25
Cu(3)	8e	0.25
Cu(4)	16h	0.25

Table XIII

Final Positional and Thermal Parameters^{a,b}
for CuBrTe

I

Positional and Isotropic Thermal Parameters

Atom	x	y	z	B
Te	0.1429(2)	0.0	0.0	-
Br	0.0	0.1158(4)	0.6201(16)	-
Cu(1)	0.3591(18)	0.6219(18)	0.8714(105)	1.58
Cu(2)	0.0	0.25	0.2815(130)	4.38
Cu(3)	0.0	0.25	0.8403(207)	2.90
Cu(4)	0.0	0.3200(41)	0.1217(154)	8.58

Table XIII - continued

Anisotropic Thermal Parameters ($\times 10^4 \text{ \AA}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te	185.7(19.1)	240.4(19.1)	313.8(23.2)	0.0	0.0	8.6(10.3)
Br	187.1(25.9)	300.5(35.5)	405.4(41.5)	0.0	0.0	-29.9(16.2)

^a The anisotropic thermal parameter is defined as:

$$f = f_0 \exp(-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$$

^b Estimated standard deviations are given in parentheses, x, y, and z are fractional coordinates.

Table XIV

Summary of Refinement for CuBrTe				
Atoms ^a	Method of Refinement	Temperature Factors	No. of Cycles	R-value
Te-16f	Blk. Diag.	Isotropic	3	0.4894
Te-16f; Br-16h	Blk. Diag.	Isotropic	5	0.2199
Te-16f; Br-16h; Cu-16g	Blk. Diag.	Isotropic	5	0.1335
Te-16f; Br-16h; Cu-16g	Blk. Diag.	Anisotropic	3	0.1276
Te-16f; Br-16h; Cu-16g(0.5); Cu-4a; Cu-4b	Blk. Diag.	Isotropic	3	0.1055
Te-16f; Br-16h; Cu-16g(0.5); Cu-8e(0.5); Cu-8e(0.5)	Blk. Diag.	Isotropic	5	0.1017
Te-16f; Br-16h; Cu-16g(0.5); Cu-8e(0.25); Cu-8e(0.25)	Blk. Diag.	Isotropic	3	0.0919
Te-16f; Br-16h; Cu-32i(0.25); Cu-8e(0.25); Cu-8e(0.25); Cu-16h(0.25)	Blk. Diag.	Isotropic	7	0.0795
"	Blk. Diag.	Iso. copper, Aniso. Te,Br	9	0.0730
"	Full Matrix	"	3	0.0657

^a The set of equivalent positions to which the atoms were assigned are indicated. Occupation factors are given in parentheses. If no occupation factor is given it is assumed to be unity.

IV RESULTS AND DISCUSSION

The tellurium atoms in CuBrTe are arranged in the same manner as in tellurium metal³¹, forming infinite spirals in the c-direction. The Te-Te distance in tellurium metal is 2.86 Å, very close to the Te-Te distance of 2.75 Å found in CuBrTe. The diameter of the tellurium helix is 2.40 Å in tellurium metal as compared to 3.52 Å in CuBrTe. The tellurium spirals are alternately right and left handed, being related by mirror planes parallel to the c-axis (see Figures 5 and 6).

The bromine atoms in CuBrTe form tetrahedra. These tetrahedra are dispersed between the tellurium spirals. The tetrahedra centered at $y=1/4$ are rotated 90° to those located at $y=3/4$ (see Figures 5 and 6).

There are two basic types of positions found for the copper atoms. The coordinates determined for the two sets of 8e and the set 16h fall in the center of the bromine tetrahedra (Figure 7). The occupancy factors found for these sets of positions account for eight of the sixteen copper atoms in the unit cell. Since there are four of these bromine tetrahedra in the unit cell there must be two copper atoms located in each one. That is, in each bromine tetrahedra there are eight proposed "metastable" copper positions. In any one of these sets of eight there will be found two copper atoms. One of these coppers is probably on one of the sites near the "top" of the tetrahedron

Figure 5

Tellurium and bromine atoms in CuBrTe
unit cell showing the location of
copper atom types 1 and 2.

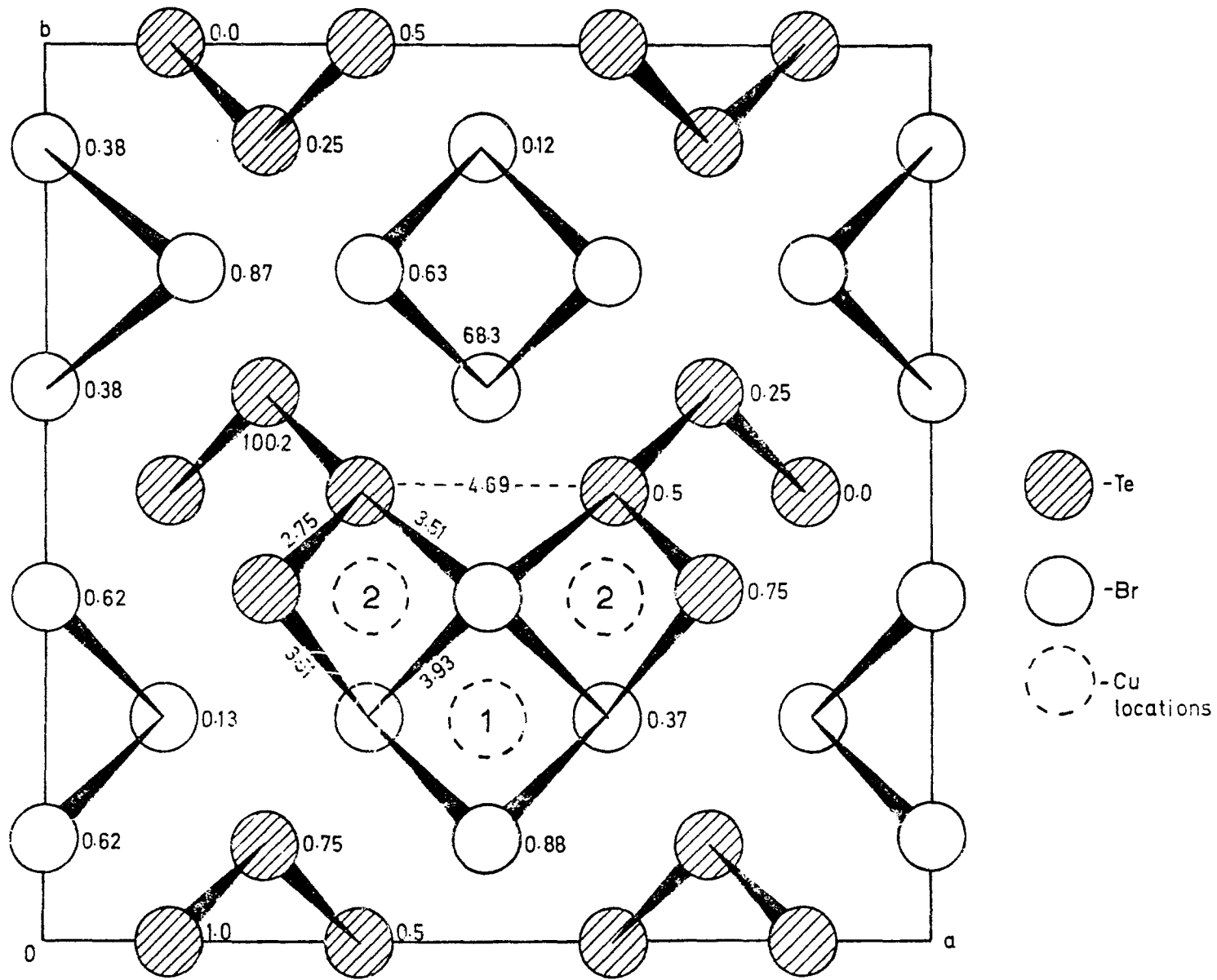


Figure 6

Trimetric projection of unit cell
of CuBrTe showing spacial relationship
of Te and Br atoms.

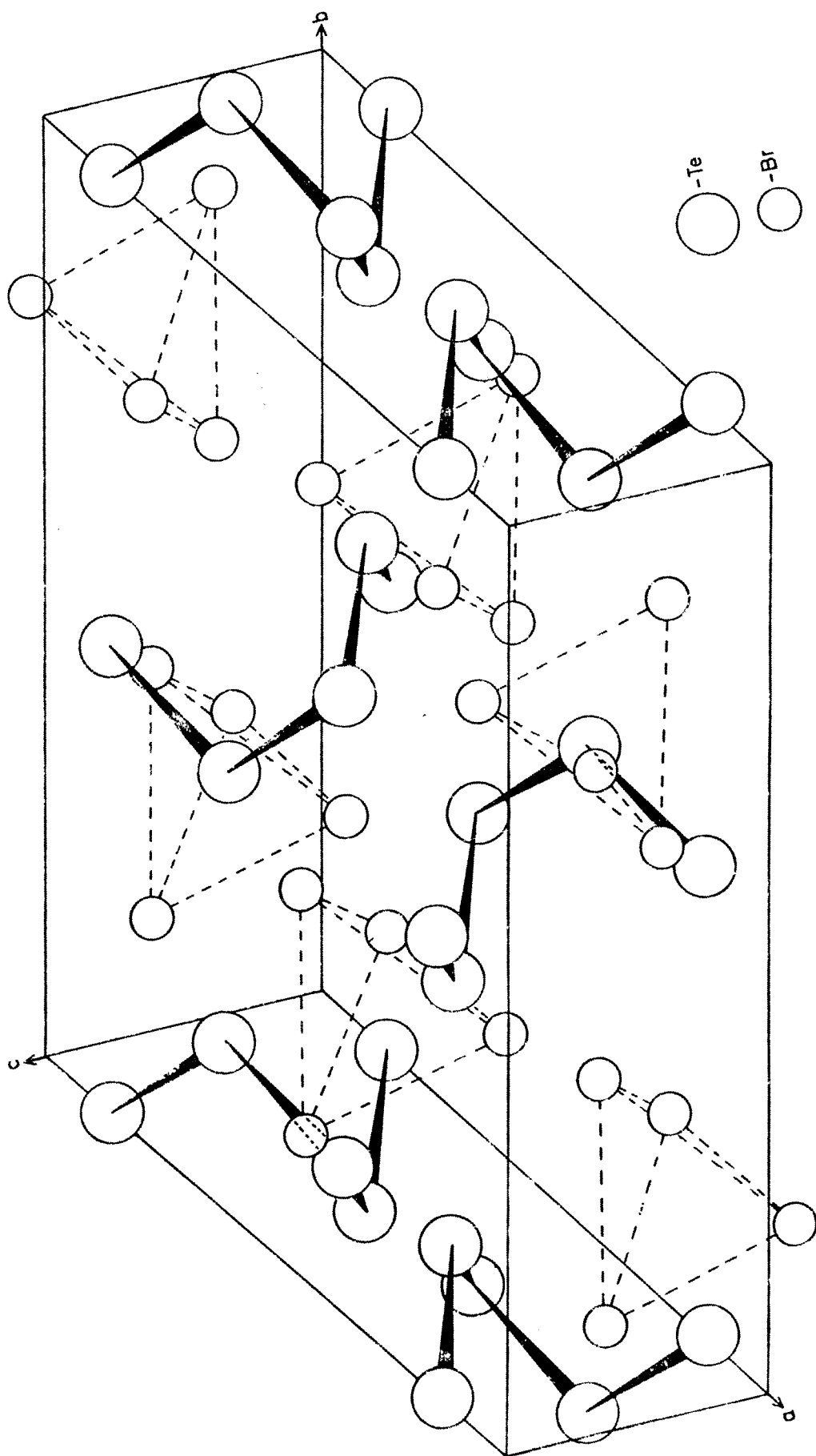
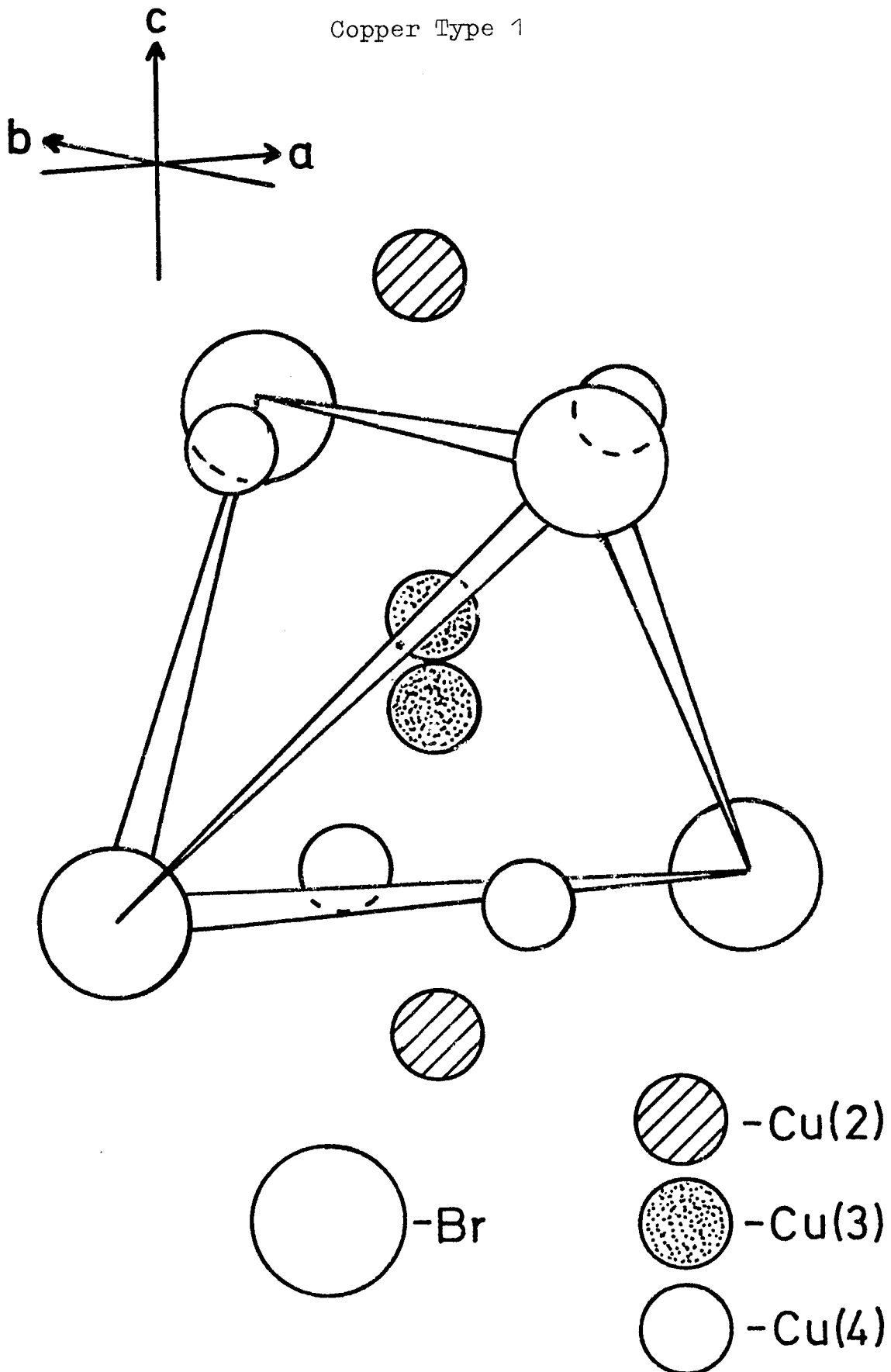


Figure 7
Copper Type 1



and the other near the "bottom" (Figure 7). These copper positions will be referred to as "type 1".

The second kind of position occupied by copper is that resulting from the coordinates determined for the set 32i with occupation factor equal to 0.25. These positions fall between the tellurium spirals and the bromine tetrahedra in a distorted tetrahedral environment. These coppers have two tellurium and two bromine atoms as nearest neighbors (Figure 8). This set of positions accounts for the other eight copper atoms. These "type 2" positions consist of sixteen pairs of possible locations. In a given unit cell there will be a copper atom located on eight of these sites.

As can be seen from Figure 5, the unit cell when viewed along either the a or b axis contains sheets or planes of tellurium and bromine atoms parallel to the c-axis. Planes of tellurium atoms and planes of bromine atoms alternate and are separated by a sheet of atoms consisting of both tellurium and bromine atoms. Pertinent bond lengths and angles are summarized in Table XVI.

The first type of disordered copper location is very similar to the average structure of β -CuBr and α -CuI proposed by Hoshino, et al.^{32,33}. It was proposed for the CuBr system that copper was statistically distributed on four or five metastable positions at the center of the bromine tetrahedra. The number of possible positions in which two copper atoms may be found in CuBrTe is eight. Otherwise the type 1 copper atoms here are analogous to

Figure 8
Copper Type 2

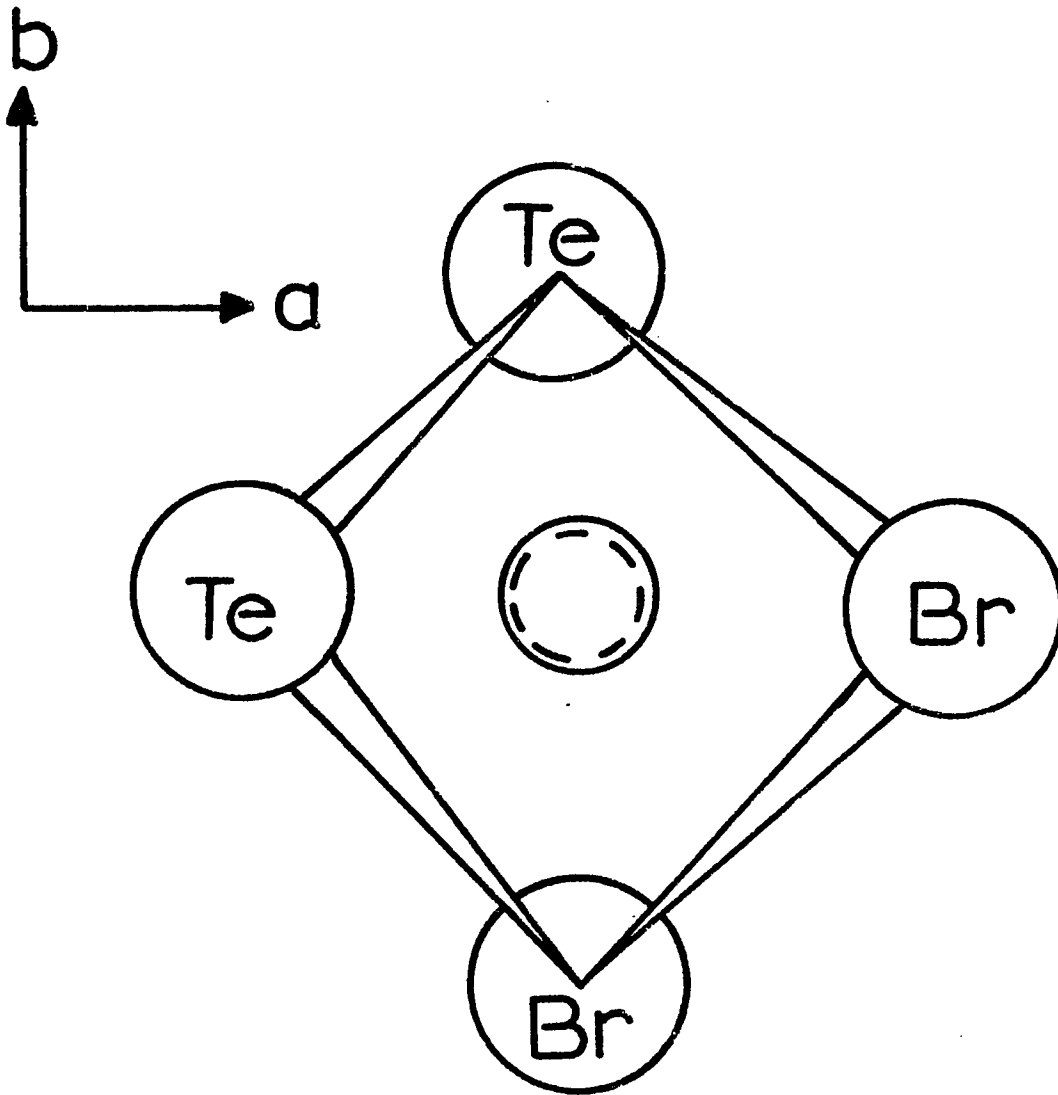


Table XVI

Bond Distances and Angles in CuBrTe

Te-Te ^a	2.751(3)	Å
Te-Br	3.511(5)	
Br-Br	3.933(8)	
Te-Cu(32i)	2.659(39)	
Br-Cu(32i)	2.593(35)	
Br-Cu(8e ₁) ^b	2.241(20)	
Br-Cu(8e ₂)	2.434(42)	
Br-Cu(16h)	2.587(72)	
Te-Te-Te ^a	100.2°	
Br-Br-Br ^c	68.3	

^a in the tellurium spiral

^b subscripts distinguish the two 8e copper positions

^c Br-Br-Br angle within the tetrahedron

the situation observed by Hoshino. Similar situations were found to exist in α -CuI and α -AgI^{34,35}.

The author has found no literature reference to the specific situation analogous to the second type of copper atom being proposed here.

The overall structure of CuBrTe, then, may be viewed as that of tellurium metal with the spirals separated by insertion of copper and bromine atoms. The distance of closest approach of tellurium spirals here is 4.69 Å as compared to 3.74 Å in tellurium metal. The various Cu-Br distances are very close to that for CuBr (2.459 Å).

As can be seen from the diagrams, the coordinates found for the type 1 coppers (8e,8e,16h) produce positions which fall close together in groups in the center of a tetrahedron formed by bromine atoms. Analogously, the coordinates found for the copper atoms on 32i define pairs of positions which have been called type 2. When more than one specific location is found for a given atom, the structure is said to be disordered with respect to that atom. Here we are proposing that these positions are sites in which the copper atoms may be found as opposed to assigning one specific site for each atom, as is the case for the tellurium and bromine atoms.

As was mentioned in the previous section, refinement was tried using sets of positions which yield points that are the average of these pairs or groups. For example, 16g instead of 32i, sets of four in place of sets of eight. The agreement was not as good and the isotropic temperature

factors were generally very large, compared to the final temperature factors.

Abnormally high temperature factors are characteristic of structures containing disordered atoms³⁶. The implication is that copper atoms can be found in positions spread over a much larger area than is reasonable on the basis of vibration alone. That is, there are several positions in the center of the bromine tetrahedra (copper type 1) at which the copper atom may be found. The positions are probably statistically occupied. Also, for copper type 2 there are two positions at which the copper atom may be found. These might be statistically occupied or systematically alternated in adjacent unit cells, perhaps leading to a larger unit cell than was observed.

Another effect which has been observed as the result of deviation from perfect order in a crystal is an overall reduction in diffraction intensities³⁷. The intensities observed in this work were extremely weak. The overall scale factor necessary to bring the observed intensities to an absolute scale based on the scattering powers of the atoms involved was over twenty.

From primary valence considerations these compounds are novel in that one would not predict bonding between the three species Cu^{+1} , Br^{-1} , and Te^0 . The observation that the structure consists of a tellurium lattice with copper and bromine interspersed makes sense. The previous observation of disorder of the first type lends credibility to these results. The "metastable" type 2 positions in which

copper is being proposed could be simply due to the fact that it is not bound strongly to tellurium. That is, there is more than one place in which the copper atom will fit without strain.

Fortunately for the crystallographer most crystal structure determinations are well behaved in that the atoms can all be assigned a specific location. Structures such as this one where assignments can not be made definitely, however, are not uncommon and some times cannot be solved satisfactorily³⁸. The author feels that a satisfactory solution has been achieved, given the data available. The agreement ($R=0.066$) obtained between the calculated and observed structure factors is quite good. This indicates that the model being proposed has to be very close to the actual situation.

After the apparent disorder of the copper atoms was found a very long rotation photograph was taken about the c-axis. This photograph showed very faint layer lines interspersed at intervals of one third of the original layer lines. If these layer lines represent the true lattice dimension the c dimension would be three times as long as the one used here. This could be indicative of a superlattice or polytype which could explain what appears to be disorder³⁸. The polymeric tellurium lattice (infinite spirals) could provide the host for polytypes in structures of this type. Analogous situations exist in which infinite sheets of one atom are present and the other atom or atoms pack in the interstitial sites in alternate patterns to form polytype

structures. An example of this behavior is TaS_2 ³⁹. This possible explanation of our observations should be investigated further.

In the introduction it was noted that the copper chalcogenide halide compounds were all semiconductors. Materials can be made semiconducting by the introduction of impurities or defects to their crystalline lattice⁴⁰. The semiconducting nature of intrinsic semiconductors can also be enhanced by introduction of such impurities or defects⁴¹. It is felt by the author that the disorder observed in CuBrTe could be an explanation for its semiconducting nature. The disordered copper atoms may be thought of as being "Frenkel-like" defects. That is not to say they are strictly Frenkel defects where the atom is completely removed from its ordered site and found in an interstitial vacancy. One can think of the copper atom being removed from its ideal position and located in one of the several alternate positions proposed, leaving in effect a vacancy.

Preliminary crystallographic studies indicated that the three compounds CuClTe , CuBrTe , and CuITe were isostructural². They were found to be of the same symmetry and space group. The results of this work indicate that complete crystallographic structure determinations for the other members of this series would be worthwhile. The disorder in copper observed here may or may not be present in the other two. The radii for the halogens in these other two compounds fall on either side of that for bromine in

CuBrTe. It would be interesting to see if packing considerations are responsible for the type 2 copper observed. It seems reasonable that the likelihood of seeing the type 1 disorder in CuClTe and CuITe is quite high.

It would also be interesting to look at the intensity data for a crystal grown by another method to see if the method of synthesis influences the order of the structure, and to determine the structures of other compounds of different stoichiometry.

Since the gold compounds did not have tellurium spirals the factors that influence spiral formation and molecular packing should be determined.

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