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The crystal structure of bismuth monochloride

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THE CRYSTAL STRUCTURE OF BISMUTH MONOCHLORIDE

by

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To the memory of my father whose exemplary life and untimely martyrdom provided the original stimulus and

To my mother who sentenced herself to ten years of solitude in order that I may attain this height of academic achievement.

INTRODUCTION

The Problem--Solution of Bismuth in Liquid Bismuth Trichloride

Solutions of metals in their molten salts are of current interest because of unanswered questions concerning the mechanism of solution and the type of species which are formed. Contributions to a better understanding of these solutions have been made through measurements of vapor pressures, phase equilibria, freezing point depressions, electrical properties, and absorption spectra. Still, the species and equilibria in solution are not defined adequately and there exist at present almost as many pet theories as there are men of science who have given of their time and effort to the problem.

The three principal models currently being considered for solution mechanism involve the formation of (1) neutral metal atoms or molecules, (2) metal ions plus solvated electrons, or (3) reduced ions or molecules. The last view, credited with the greatest degree of support, has been championed vigorously by Corbett (Corbett et al., 1957; Corbett, 1961). The Bi-$BiCl_3$ system is of particular interest in this connection because the reduced salt, identified as bismuth monochloride*

*The term "bismuth monochloride" and the symbol BiCl will be used throughout this work for the sake of convenience to designate the compound whose crystallographic formula turns out to be $BiCl_{1.17}$.

precipitates out of solution as a solid phase.

Cubicciotti, the major exponent of the first two theories (Cubicciotti, 1952, 1960a; Keneshea and Cubicciotti, 1958), argued that positive deviations from Raoult's law in the $Bi-BiCl_3$ system deny the existence of individual lower valent ions in solution (Cubicciotti et al., 1958). He acknowledged, however, that reduced polymeric ions like Bi_n^{+m} would fit his data for the vapor pressure of Bi dissolved in $BiCl_3$. According to Cubicciotti, Bi atoms or ions, upon solution, enter the octahedral holes in the quasi-lattice of the molten chloride.

The cryoscopic data of Mayer et al. (1960) indicated Bi_2Cl_2 as the principal constituent of moderately concentrated solutions near the $BiCl_3$ liquidus curve. Concurrently, Bredig (1959) proposed the presence of both the Bi_2 and Bi_2Cl_2 species, with the former becoming more prevalent at high temperatures, to reconcile the vapor pressure and cryoscopic results. Yosim et al. (1959) noted that the presence of neutral dimers or Bi_2^{++} ions is consistent with electrical conductivity, vapor pressure and magnetic susceptibility measurements. They also pointed out, however, that no single species or mechanism is sufficient to explain the entire phase diagram and particularly the retrograde solubility above the syntectic temperature.

More recently, Topol et al. (1961) studied the $Bi-BiCl_3$

system by e.m.f. measurements. They observed a Nernst n = 2, corresponding to the species BiCl, at low metal concentrations (N_2 < .01), whereas slightly higher concentrations yielded n values of 6 and even 8. The authors concluded that both BiCl (or Bi^+) and Bi_4Cl_4 are likely to be present in solution, the latter becoming predominant with increasing Bi concentration. The presence of other species such as Bi_2, Bi_3Cl_3 and Bi_3^+ was not excluded.

Interpretation of thermodynamic data in fused salt systems for the purpose of identifying the species formed involves broad assumptions about such concepts as activity coefficients and formation of solid solutions and it is not surprising that attempts along this line have met with rather limited success. The more direct, physical methods have been showing greater promise. Already the discovery of the diamagnetic character of these solutions has narrowed considerably the range of possible species.

More recently, two structural studies made significant contributions to the available evidence. Measurement of the visible absorption spectra by Boston and Smith (1960) provided first direct evidence for the existence of two species in solution. Although these have not been positively identified, it appears that the species prevalent at very low bismuth concentrations (0.01 M) was the Bi atom or the Bi^+ ion. This is consistent with Holecek's (1953) observation that magnetic

susceptibility increases with decreasing metal concentration in this concentration region. The second study, by Levy et al. (1960), in the form of x-ray diffraction on molten and crystalline $BiAlCl_4$ apparently indicates the presence of Bi_3^{+3} ions in both phases.

Although no definite conclusions have been reached at this stage, certain general notions have transpired. The formation of several reduced species has been pretty well established. Furthermore, it appears very likely that these species are Bi^+ or BiCl at very low metal concentrations with some degree of polymerization taking place as the bismuth content is increased. An approach more direct and complete than any tried before was definitely indicated at this stage. Just as inspection of fossilized remains in ancient rocks gave man his first glimpse of early life forms, vital clues to the nature of the solute species were expected from a study of their frozen equilibrium in a crystal structure.

The Story of BiCl and Related Compounds

In 1908, Eggink presented the first substantial characterization of the Bi-$BiCl_3$ system in the form of a phase diagram. He observed that when the two-liquid phase obtained with excess metal was cooled, an intermediate solid phase separated at a temperature higher than the melting point of either component. Eggink's claim of isolating BiCl by

ether extraction of the trichloride from the mixture has since been questioned by Corbett (1958).

Some 40 years later, Sokolova (1952) redetermined the Bi-$BiCl_3$ phase diagram and, subsequently, reported x-ray and microstructure observations on the system, (Sokolova et al., 1954). With the aid of powder patterns she detected the new phase in quenched Bi-$BiCl_3$ solutions and claimed for it the BiOCl structure on the basis of similar intensity distributions.

The third and most thorough study was due to Yosim et al. (1959) who published the complete phase diagram for the system. As Eggink and Sokolova before them, they recognized the presence of an intermediate phase with an approximate BiCl stoichiometry but made no attempt to isolate it.

The elusive monohalide was finally cast into the limelight by Corbett (1958) who isolated the compound and described its properties in some detail. Subsequently, Darnell and Yosim (1959) presented a thermodynamic characterization of solid BiCl and Cubicciotti (1960b) reported equilibrium data for BiCl gas. Corbett's preliminary powder pattern data agreed well with those deduced by Holecek (1953) but bore little resemblance to the patterns reported by Sokolova et al. It appears likely that the presence of hydration and hydrolysis products was responsible for the discrepancy and for the presence of BiOCl lines in her powder

patterns. On the basis of certain properties of BiCl such as its diamagnetic character and the high viscosity of its solutions, Corbett predicted cyclic polymerization in the crystal.

Wolten and Mayer (1958) were able to index powder patterns of $BiCl_3$ on the basis of a primitive cubic unit cell with a_o = 8.14 Å and space group $P2_13$. Concurrent calculations based on BiCl powder patterns led Wolten* to claim a hexagonal unit cell for the monohalide. In the vapor phase, $BiCl_3$ was found to consist of pyramidal molecules with a Bi-Cl bond length of 2.48 Å and a Cl-Bi-Cl angle of ~ 100° (Skinner and Sutton, 1940). Levy et al. (1959) found from x-ray diffraction studies of molten, polycrystalline and monocrystalline $BiAlCl_4$ that the Bi atoms apparently form equilateral triangles with a Bi-Bi bond length of 3.04 Å. Solid $BiAlCl_4$ crystallizes in the rhombohedral system with a_o = 12.12 Å, α = 58°23', Z = 6 and space group R3c, which conveniently accommodates 2 Bi_3^{+3} units.

In closing, mention should be made of the compound $Bi_{24}O_{31}Cl_{10}$ for which the chief connection with this work lies in its outsized unit cell. An idealized model for this structure was proposed by Sillen and Edstrand (1942). The model featured 24 Bi atoms in a unit cell of approximately 30 x 10 x 4 Å. Bi-Cl bond lengths of 3.30 Å and 3.45 Å were measured.

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*Wolten, G. M., Atomics International, Canoga Park, California. Powder patterns of BiCl. Private communication. 1958.

EXPERIMENTAL PROCEDURE

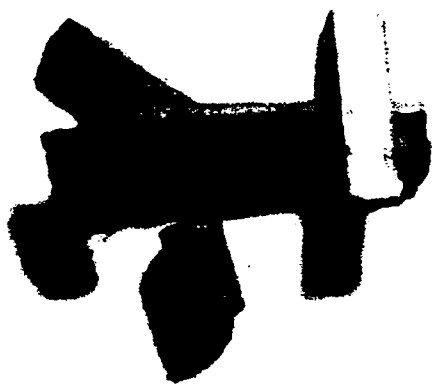
Preparation of Crystals

Preparation of bismuth monochoride has been described by Corbett (1958). Mixtures containing up to 76% BiCl were synthesized by equilibration of $BiCl_3$ with excess metal at 325° in a sealed Pyrex tube, followed by the reduction of temperature to 270° over a period of one to two weeks. Each time, the tube was opened in an inert atmosphere and single crystals of BiCl projecting from the matrix were picked out manually. Over 100 crystals were obtained in this manner.

BiCl crystallizes in the form of shiny black prisms with a flattened hexagonal cross section. Upon contact with the atmosphere, signs of surface decomposition became evident within two days. After 10 days of exposure, deterioration of the crystals had progressed to the stage where diffraction would be no longer practical. Figure 1 shows some of the larger specimens found. The surfaces bear traces of the hydrolyzed matrix which was removed during the shaping operation.

Because of the high absorption coefficient of Bi atoms, the crystals had to be ground into regular shapes in order that a convenient and accurate absorption correction could be applied to the observed diffraction intensities. Cylindrical shapes were attained by rolling crystals over fine emery

Figure 1. Crystals of BiCl; the largest specimen measures 136 x 368 x 1670μ



paper with the bare finger. One of these cylinders is shown in Figure 1. Spheres were prepared with the aid of a circular abrasive track patterned after Bond (1951).

Some 25 cylindrical and spherical crystals of diverse size and degree of regularity were mounted in hand drawn, evacuated capillaries. This precaution insured that all diffraction data could be taken with the same crystal. Preliminary Weissenberg photographs were taken of each crystal and the most suitable specimen was selected on the basis of dimensional uniformity, intensity and neatness of reflection spots, and alignment with the axis of rotation. Spheres were rejected en masse because they produced weak reflections with extensive smudging.

Optimum thickness for the diffraction specimen was originally calculated according to Buerger's (1942, p. 180) formula $t = 2/\mu$, where t is the thickness of the crystal and μ is the linear absorption coefficient. The value $t = 2/1513 = .0013$ cm, thus obtained, was found unsatisfactory during the preliminary diffraction exposures and a cylinder .0320 cm long with a diameter of .0098 cm was eventually selected.

Determination of Density

Determination of the experimental density of BiCl presented a special problem because the crystals were too heavy for the floatation technique and too scarce for the macro-

pycnometric method. Corbett* had obtained a macro-pycnometric value of 6.54 g/cc by measuring the density of a BiCl-$BiCl_3$ mixture and correcting for a small trichloride impurity. Since this value did not agree with the assumed stoichiometry of the crystal, it was decided to experiment with two other more direct approaches.

The dimensions of seven of the largest regularly shaped crystals were carefully measured under a binocular microscope and their weights were determined on a microbalance by Mr. Robert Bachman of the Ames Laboratory. Their average density of 6.05 g/cc was considered unreliable because of considerable variation among individual determinations and the likelihood that surface imperfections made this value too low.

Subsequent efforts to measure density by weighing crystals in air and in heavy liquid failed, giving way to the development of a micropycnometric approach which offered very good precision while requiring only several milligrams of material. The apparatus employed in the micropycnometric technique is shown in Figure 2. The micropycnometer can be conveniently manufactured from capillary tubing. After its volume had been determined by the conventional method, the

*Corbett, J. D., Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Determination of the density of BiCl. Private communication. 1958.

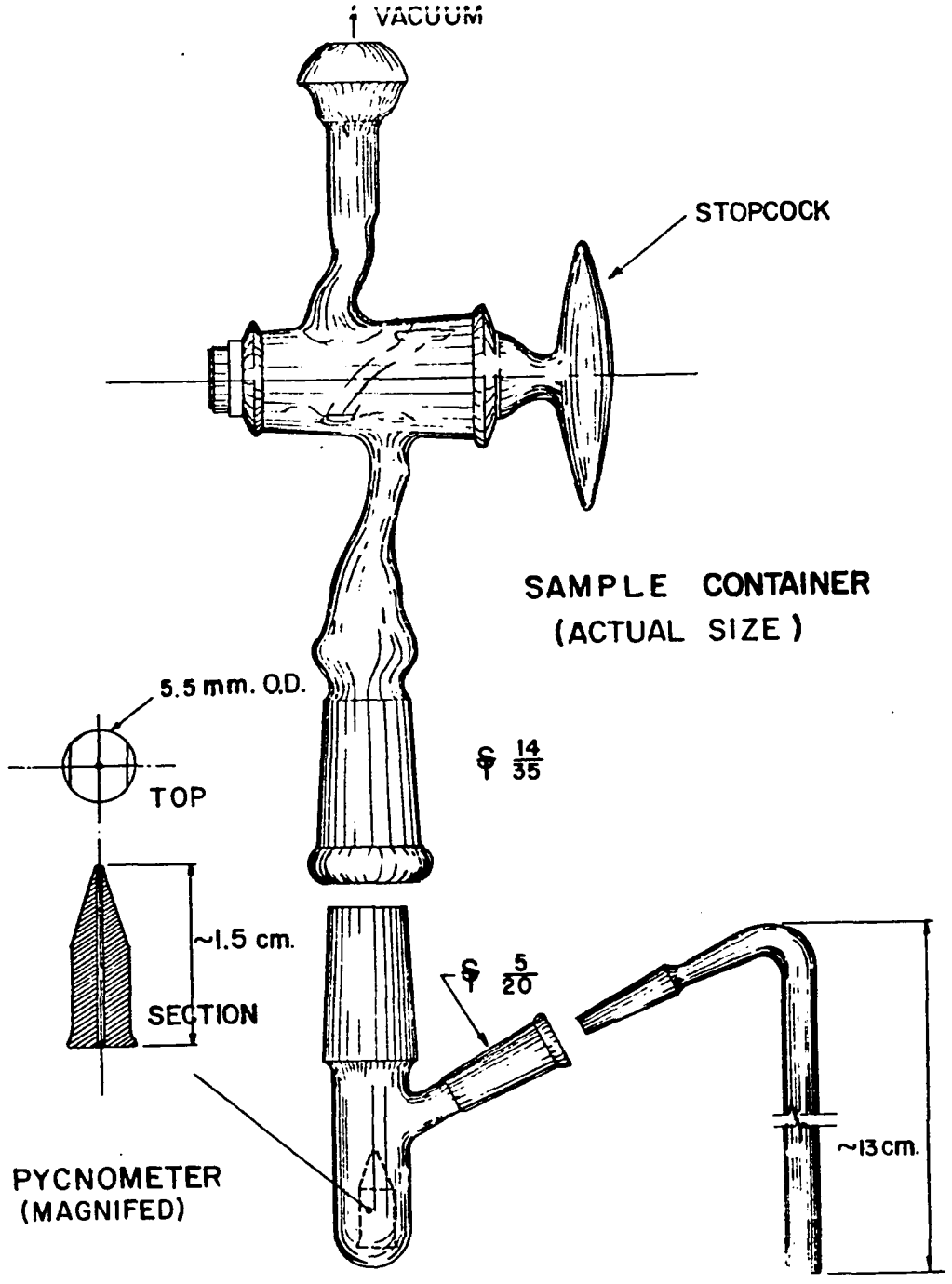


Figure 2. Micropycnometric density apparatus

pycnometer was cleaned, weighed on a microbalance, loaded with crystals, and reweighed. This assembly was then placed in the sample container and the side arm was filled with 1-bromonaphthalene, selected for its low vapor pressure and chemical inertness. The density of 1-bromonaphthalene was measured with the same pycnometer, and found to be 1.4997 $\pm$ .003 g/cc at 25° as compared with the literature value of 1.4785 g/cc (Jones and Lapworth, 1914). The sample container was evacuated to remove all traces of air from the crystals and liquid alike, following which 1-bromonaphthalene was allowed to enter the pycnometer by turning the side arm upward. In the last step, the micropycnometer containing crystals and liquid was removed from the sample container, wiped clean, and weighed.

Calculations were carried out according to the formula

$$\rho_c = \frac{w_c}{V_p \rho_l - w_{c+l} + w_c} \rho_l$$

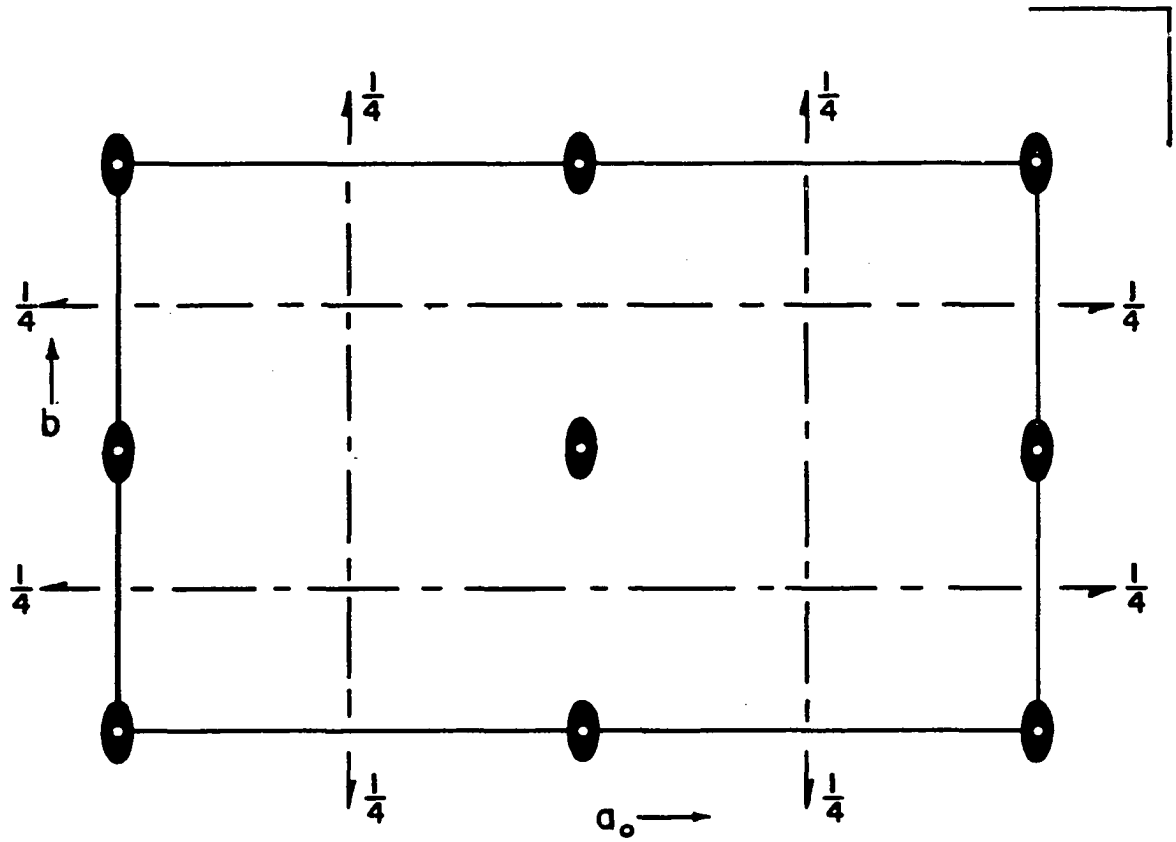
where the symbols ρ, w, and v denote density, weight, and volume and the subscripts p, c, and l refer to pycnometer, crystals, and liquid, respectively. Individual determinations were made on five batches of crystals. Their average value of 6.54 $\pm$ .05 g/cc was identical with Corbett's result and was accepted as the true density of BiCl.

Diffraction Data

Preliminary Weissenberg and precession photographs indicated an orthorhombic unit cell. Lack of systematic extinctions for the hkℓ and hk0 data in conjunction with the extinction conditions $h + \ell = 2n + 1$ for h0ℓ data and $k + \ell = 2n + 1$ for 0kℓ data, allowed the choice of space groups Pnn and Pnnm. Figure 3 illustrates the location of symmetry elements in space group Pnnm and lists the general coordinates of the two symmetry sets allowed by extinction rules.

Precision lattice constants were measured by the conventional Weissenberg back reflection method (Buerger, 1942) using unfiltered Cu, Cr, and Co radiation. Their values were $a_o = 23.057 \pm .002$ Å, $b_o = 15.040 \pm .007$ Å, c_o (the needle axis) $= 8.761 \pm .003$ Å. On this basis, 48 BiCl molecules per unit cell were most likely, resulting in a calculated density of 6.41 g/cc.

All intensity data were taken with Cu Kα radiation. A molybdenum target could not be used because it produced fluorescence in bismuth. Multiple film Weissenberg photographs were taken for layers hk0, hk1, hk2, hk3, hk4, hk5 by the equi-inclination technique (Buerger, 1942). Exposure times varied between 120 and 180 hours. Precession exposures of 2, 4, 8, 16, and 32 hours were taken of layers h0ℓ, h1ℓ, and 0kℓ in order to supplement the Weissenberg data at low



8 — FOLD POSITIONS

$x,y,z;\ \bar{x},\bar{y},z;\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}-z;\ \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}-z;$

$\bar{x},\bar{y},\bar{z};\ x,y,\bar{z}\quad \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z;\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2}+z;$

4 — FOLD POSITIONS

$x,y,0;\ \bar{x},\bar{y},0;\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2};\ \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}.$

Figure 3. Symmetry elements and general coordinates of space group Pnnm

angles.

Weissenberg films were judged visually against series of standard spots prepared separately for each layer to allow for wear and changing spot shape. The film factor was checked against visual observations and adjusted in accordance with spot intensity. Reflections appearing on different films in a pack were double checked until their observed values agreed within 10% or less. For each layer, uniform portions of the reciprocal lattice were exposed on a single film pack to provide a basis for converting all Weissenberg intensities to the same relative scale. Precession reflections were judged against a selected spot appearing on the h0ℓ films. These were subsequently brought in line with the rest of the data by comparing intensities of reflections common to Weissenberg and precession films. In all, 1938 observed reflections were judged. The 566 unobserved reflections, which were not subject to systematic extinctions, were assigned a value equal to 60% of the lowest observable intensity for that layer. Table 1 lists the number of reflections obtained for each layer.

Treatment of Intensities

Before the observed intensities could be used in structure determination, they had to be corrected for the Lorentz factor, polarization, absorption, and multiplicity.

Lorentz and polarization corrections were applied to the

Table 1. Number of reflections

Layer	Weissenberg Reflections observed	Weissenberg Reflections unobserved	Precession reflections	Total reflections
hk0	357	89	3	449
hk1	338	101	6	445
hk2	330	103	5	438
hk3	312	106	3	421
hk4	308	81	4	393
hk5	287	68	3	358
Total	1932	548	24	2504

Weissenberg intensities by means of the I.B.M. 650 computer using INCOR-IM, a locally-modified version of the INCOR-I program (Zalkin and Jones, 1957). Precession data were handled with the aid of Olson's* correction program.

A new approach to the calculation of absorption corrections was recently presented by Bond (1959) ending Bradley's (1935) 24 year hegemony in this field. Figure 4 illustrates the marked discrepancy between the two treatments. An absorption correction and sharpening (ACS) program, based in part on Bond's paper, was written for the I.B.M. 650 computer.

*Olson, D. H., Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa. Correction program for precession intensities. Private communication. 1960.

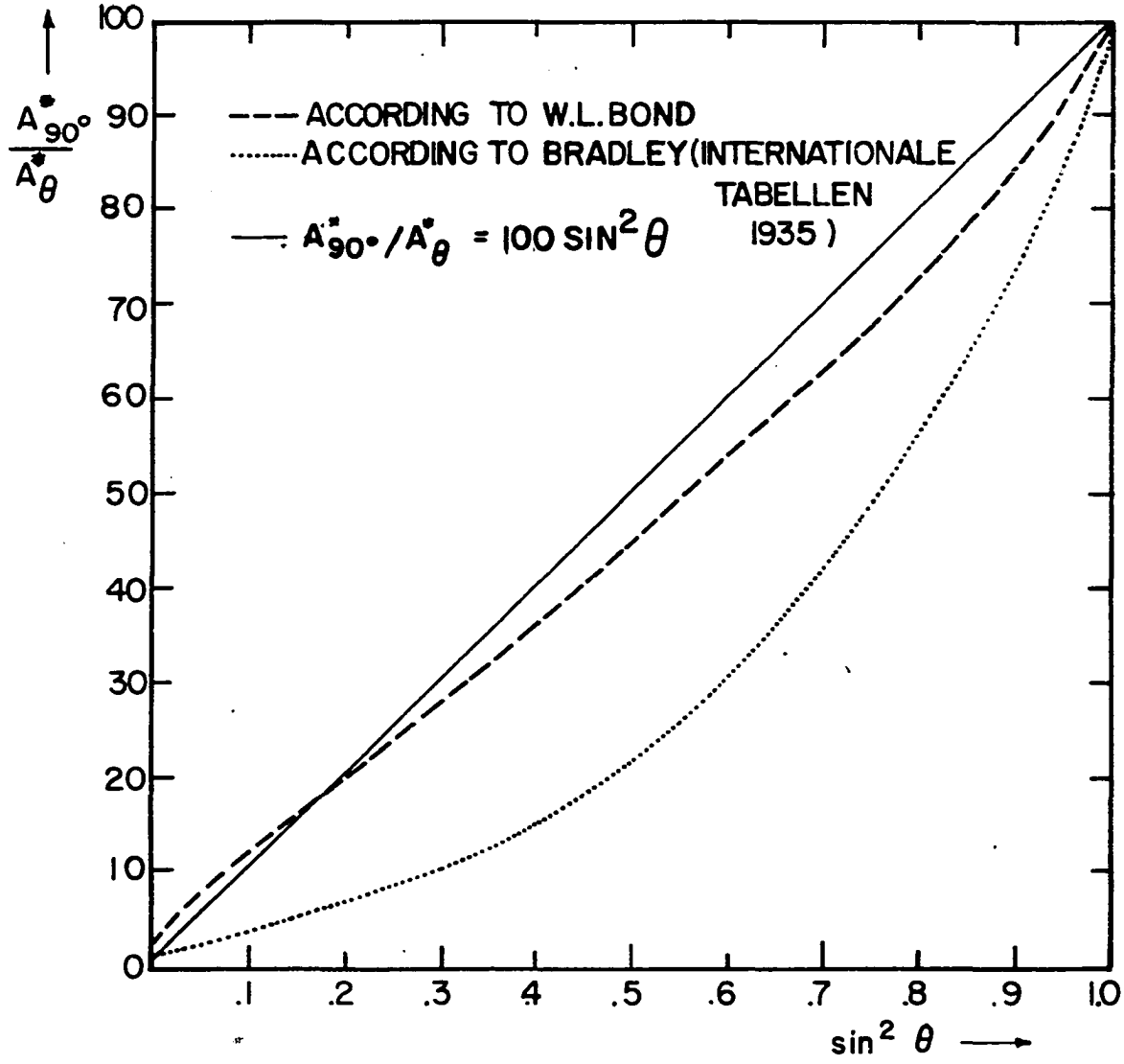


Figure 4. Absorption correction plots; μR = 8.0

The program is designed to apply absorption corrections to Weissenberg data from cylindrical and spherical crystals and to "sharpen" intensities according to the method proposed by Patterson (1935) and developed by Lipson and Cochran (1957, p. 170). A detailed program writeup is given in Appendix A.

Absorption corrections are listed in Bond's paper as a function of θ and μR, where θ is the Bragg angle and μ is the linear absorption coefficient. R is defined by the relation

$$R = R_o \sec \nu,$$

where ν is the angle between the incident x-ray beam and a plane normal to the cylinder axis. In the present case, $\mu = 1513\ cm^{-1}$ and $R_o = 9.8 \times 10^{-3}$ cm, so that $R = 7.4 \sec \nu$.

Plots of absorption correction *vs.* $\sin^2\theta$ were prepared for different values of μR, as required by the program, and corrected intensities were computed for all Weissenberg reflections by means of the ACS program. Absorption-corrected precession intensities were read off a plot of W_{LPA}/P_{LP} *vs.* $\sin^2\theta$, where W and P stand for Weissenberg and precession intensities and L, P, and A indicate that the Lorentz, polarization, and absorption corrections have been applied. The conversion of all intensities to the same scale took place during this step.

Division by the appropriate multiplicity factors was accomplished during the routine operations prior to the summation of the Fourier series.

STRUCTURE DETERMINATION

The approach to structure determination was based on the "heavy atom" technique. This assumes that the correct assignment of bismuth positions will establish the phase angles of most large reflections and thus lead to the determination of chlorine positions by Fourier methods.

Trial structures were based on interpretation of Patterson vector maps. Conventional and difference Fourier maps were employed to locate chlorine atoms.

Vector Maps

The general form of the Patterson function is

$$P(XYZ) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{\ell=-\infty}^{\infty} F(hk\ell)^2 \exp 2\pi i(hX+kY+\ell Z),$$

where X, Y, and Z designate grid points of the unit cell rather than atomic coordinates, V is the volume of the unit cell, and F is a quantity to be discussed later, known as the structure factor. In space group Pnnm, the relation $F(hk\ell) = F(\bar{h}k\ell) = F(h\bar{k}\ell) = F(hk\bar{\ell})$ holds for all reflections. Consequently, the above expression reduces to

$$P(XYZ) = \frac{8}{V} \sum_{h} \sum_{k} \sum_{\ell=0}^{\infty} F(hk\ell)^2 \cos 2\pi hX \cos 2\pi kY \cos 2\pi \ell Z$$

or, more specifically, to

$$P(XYZ) = \frac{1}{V} F^2(000) + \frac{2}{V} \left[\sum_{h=1}^{\infty} F^2(h00) \cos 2\pi hX + \sum_{k=1}^{\infty} F^2(0k0) \cos 2\pi kY + \sum_{\ell=1}^{\infty} F^2(00\ell) \cos 2\pi \ell Z \right]$$

$$+ \frac{4}{V} \left[\sum_{h} \sum_{k=1}^{\infty} F^2(hk0) \cos 2\pi hX \cos 2\pi kY + \sum_{h} \sum_{\ell=1}^{\infty} F^2(h0\ell) \cos 2\pi hX \cos 2\pi \ell Z + \sum_{k} \sum_{\ell=1}^{\infty} F^2(0k\ell) \cos 2\pi kY \cos 2\pi \ell Z \right]$$

$$+ \frac{8}{V} \left[\sum_{h} \sum_{k} \sum_{\ell=1}^{\infty} F^2(hk\ell) \cos 2\pi hX \cos 2\pi kY \cos 2\pi \ell Z \right].$$

As the first step, a sharpened hk0 Patterson projection was computed and plotted since, up to that point, the only indication of the complexity of the structure was the large volume of the unit cell for a compound with an apparently simple stoichiometry. The form of the two-dimensional function is

$$P(XY0) = \frac{1}{A} F^2(000) + \frac{2}{A} \left[\sum_{h=1}^{\infty} F^2(h00) \cos 2\pi hX + \sum_{k=1}^{\infty} F^2(0k0) \cos 2\pi kY \right] + \frac{4}{A} \left[\sum_{h} \sum_{k=1}^{\infty} F^2(hk0) \cos 2\pi hX \cos 2\pi kY \right]$$

The 360 observed hk0 intensities were multiplied by means of

the ACS program by the sharpening factor $(\sum_j Z_j / \sum_j f_j)^2$ where Z_j is the atomic number and f_j, the dispersion-corrected scattering factor of atom j. The summing code specifying the evenness or oddness of indices was supplied and special reflections were divided by their appropriate multiplicity factors.

Summation was performed on the I.B.M. 650 computer using the TDF-2 program (Fitzwater and Williams, 1959). Results were tabulated on the I.B.M. 420 tabulator with the aid of a special wiring panel which expands the basic ¼ x ¼ x ¼ portion of the unit cell into the desired ½ x ½ x ½ octant. The mmm symmetry of the vector map made it unnecessary to consider the entire unit cell. A contour map of the sharpened hk0 Patterson projection is shown in Figure 5.

The vectors which these peaks represent were classified as intraset or interset according to whether they referred to atoms of the same or different symmetry sets. The mode of attack consisted of the selection of possible Bi positions on the basis of intraset vectors, and subsequent use of interset vectors for verification. The general coordinates of intraset and interset vectors, based on the four-fold set of Figure 3, are listed in Tables 2 and 3 along with their respective multiplicities.

The major peaks along the right hand edge and the upper edge of the vector map were very likely to represent in part

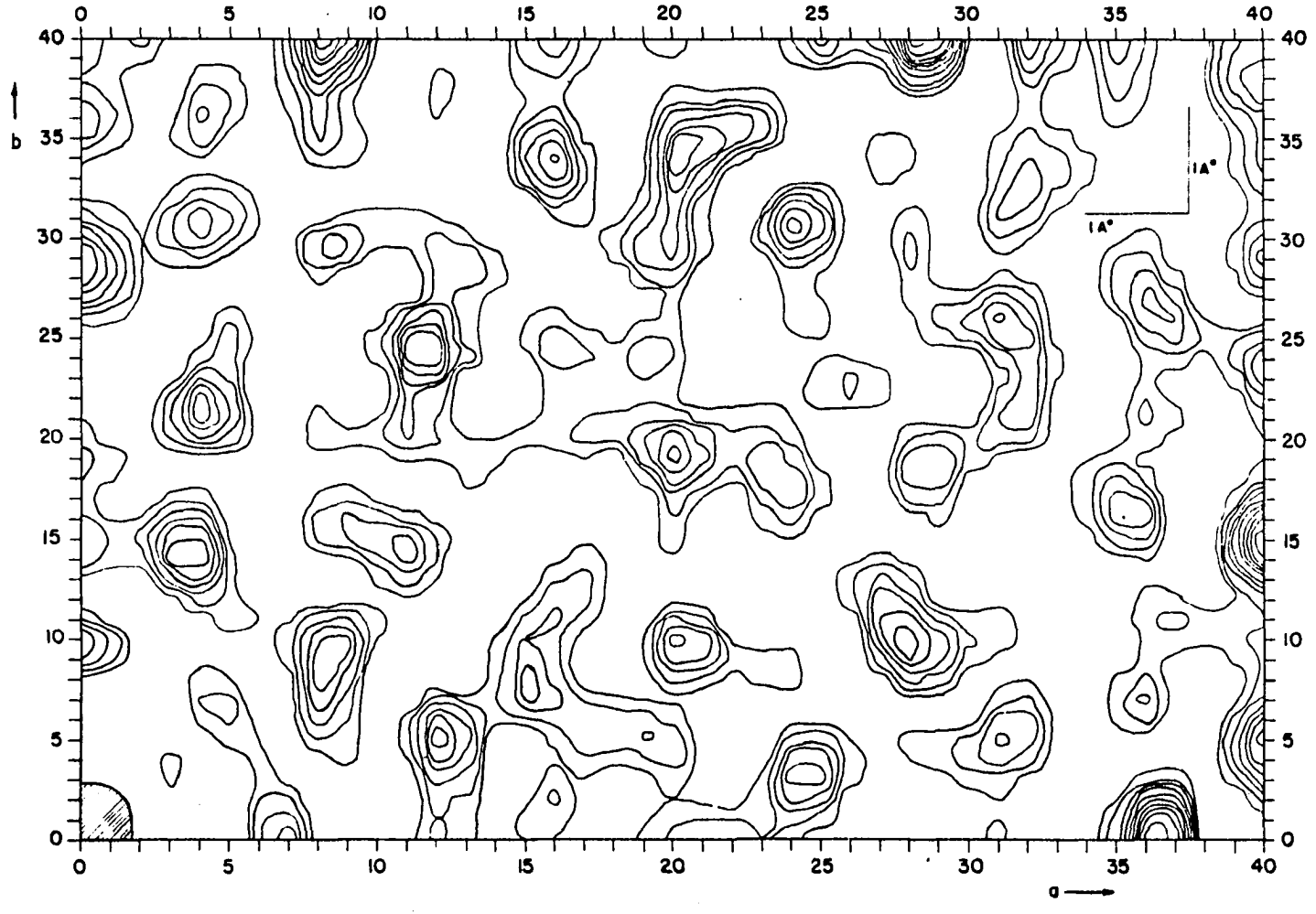


Figure 5. Sharpened Patterson projection onto the (001) plane

Table 2. Intraset vectors

Vectors			Multiplicity 8-fold	Multiplicity 4-fold
0	0	0	8	4
0	0	$\pm 2z$	4	
$\pm 2x$	$\pm 2y$	0	2	1
$\pm 2x$	$\mp 2y$	0	2	1
$\pm 2x$	$\pm 2y$	$\pm 2z$	1	
$\pm 2x$	$\pm 2y$	$\mp 2z$	1	
$\pm 2x$	$\mp 2y$	$\pm 2z$	1	
$\pm 2x$	$\mp 2y$	$\mp 2z$	1	
$\frac{1}{2} \pm 2x$	$\frac{1}{2}$	$\frac{1}{2}$	4	2
$\frac{1}{2} \pm 2x$	$\frac{1}{2}$	$\frac{1}{2} \pm 2z$	2	
$\frac{1}{2} \pm 2x$	$\frac{1}{2}$	$\frac{1}{2} \mp 2z$	2	
$\frac{1}{2}$	$\frac{1}{2} \pm 2y$	$\frac{1}{2}$	4	2
$\frac{1}{2}$	$\frac{1}{2} \pm 2y$	$\frac{1}{2} \pm 2z$	2	
$\frac{1}{2}$	$\frac{1}{2} \pm 2y$	$\frac{1}{2} \mp 2z$	2	

Table 3. Interset vectors. Δz and Σz transform to z for vectors between 8- and 4-fold sets and to 0 for vectors between 4- and 4-fold sets; each vector has a multiplicity of 2

Vectors			Vectors		
$\pm\Delta x$	$\pm\Delta y$	$\pm\Delta z$	$\frac{1}{2}\pm\Delta x$	$\frac{1}{2}\pm\Sigma y$	$\frac{1}{2}\pm\Delta z$
$\pm\Delta x$	$\pm\Delta y$	$\mp\Delta z$	$\frac{1}{2}\pm\Delta x$	$\frac{1}{2}\pm\Sigma y$	$\frac{1}{2}\mp\Delta z$
$\pm\Delta x$	$\mp\Delta y$	$\pm\Delta z$	$\frac{1}{2}\pm\Delta x$	$\frac{1}{2}\mp\Sigma y$	$\frac{1}{2}\pm\Delta z$
$\pm\Delta x$	$\mp\Delta y$	$\mp\Delta z$	$\frac{1}{2}\pm\Delta x$	$\frac{1}{2}\mp\Sigma y$	$\frac{1}{2}\mp\Delta z$
$\pm\Delta x$	$\pm\Delta y$	$\pm\Sigma z$	$\frac{1}{2}\pm\Sigma x$	$\frac{1}{2}\pm\Delta y$	$\frac{1}{2}\pm\Sigma z$
$\pm\Delta x$	$\pm\Delta y$	$\mp\Sigma z$	$\frac{1}{2}\pm\Sigma x$	$\frac{1}{2}\pm\Delta y$	$\frac{1}{2}\mp\Sigma z$
$\pm\Delta x$	$\mp\Delta y$	$\pm\Sigma z$	$\frac{1}{2}\pm\Sigma x$	$\frac{1}{2}\mp\Delta y$	$\frac{1}{2}\pm\Sigma z$
$\pm\Delta x$	$\mp\Delta y$	$\mp\Sigma z$	$\frac{1}{2}\pm\Sigma x$	$\frac{1}{2}\mp\Delta y$	$\frac{1}{2}\mp\Sigma z$
$\pm\Sigma x$	$\pm\Sigma y$	$\pm\Sigma z$	$\frac{1}{2}\pm\Sigma x$	$\frac{1}{2}\pm\Delta y$	$\frac{1}{2}\pm\Delta z$
$\pm\Sigma x$	$\pm\Sigma y$	$\mp\Sigma z$	$\frac{1}{2}\pm\Sigma x$	$\frac{1}{2}\pm\Delta y$	$\frac{1}{2}\mp\Delta z$
$\pm\Sigma x$	$\mp\Sigma y$	$\pm\Sigma z$	$\frac{1}{2}\pm\Sigma x$	$\frac{1}{2}\mp\Delta y$	$\frac{1}{2}\pm\Delta z$
$\pm\Sigma x$	$\mp\Sigma y$	$\mp\Sigma z$	$\frac{1}{2}\pm\Sigma x$	$\frac{1}{2}\mp\Delta y$	$\frac{1}{2}\mp\Delta z$
$\pm\Sigma x$	$\pm\Sigma y$	$\pm\Delta z$	$\frac{1}{2}\pm\Delta x$	$\frac{1}{2}\pm\Sigma y$	$\frac{1}{2}\pm\Sigma z$
$\pm\Sigma x$	$\pm\Sigma y$	$\mp\Delta z$	$\frac{1}{2}\pm\Delta x$	$\frac{1}{2}\pm\Sigma y$	$\frac{1}{2}\mp\Sigma z$
$\pm\Sigma x$	$\mp\Sigma y$	$\pm\Delta z$	$\frac{1}{2}\pm\Delta x$	$\frac{1}{2}\mp\Sigma y$	$\frac{1}{2}\pm\Sigma z$
$\pm\Sigma x$	$\mp\Sigma y$	$\mp\Delta z$	$\frac{1}{2}\pm\Delta x$	$\frac{1}{2}\mp\Sigma y$	$\frac{1}{2}\mp\Sigma z$

the intraset vectors $\frac{1}{2},\frac{1}{2}\pm 2y,0$ and $\frac{1}{2}\pm 2x,\frac{1}{2},0$, respectively. The positions of these peaks were thus used to compile a list of possible x and y values which were subsequently paired by checking for the presence of corresponding 2x,2y,0 peaks within the body of the map. The characteristic Patterson ambiguity due to the four possible sign combinations was resolved by arbitrarily assigning one position as the site of a reference Bi atom from the set of four which was derived from the strongest and best defined vector peaks. This fixed the origin of the unit cell and provided a basis for interset verification.

Some 40 independent positions satisfied the interset requirements listed in Table 3 with respect to the reference atom. The task at hand was to select at least five from amongst these which would satisfy all interset requirements with respect to each other as well. Six independent positions could generate the minimum number of (eight-fold) symmetry sets required.

To this end, all 40 positions were listed in table form and the presence or absence of peaks corresponding to interset vectors was noted for each pair. The search for a self-consistent group of positions was conducted according to a systematic and efficient procedure developed especially for this purpose. Still, the large degree of overlap of projected electron densities and the reduction in the number of

checks due to the lack of z parameters soon rendered the task highly impractical.

In order to overcome these handicaps, it was decided to tackle the problem via a sharpened three-dimensional Patterson map. The procedure for obtaining corrected three-dimensional data has been described in the experimental section. A total of 1956 observed reflections was used in the summation. Sharpening and other preliminary operations were performed in the manner outlined for the two-dimensional case. Computation times for the different permutations of indices and grid dimensions were calculated and the sequences h, k, ℓ and 1/80, 1/40, 1/40 were selected. Summation was again performed on the I.B.M. 650 computer using the TDF-2 program but this time the I.B.M. 407 tabulator was used to tabulate and print the results directly on a grid suitable for plotting contours. This last step saved the time of copying hundreds of thousands of electron density values by hand.

An absolute scale factor k (such that $F_o \cdot \sqrt{k} = F_c$) and an average temperature factor B (such that $f = f_o \exp -B \frac{\sin^2\theta}{\lambda^2}$) were evaluated from a plot of $\log \langle F_o^2/\Sigma f_o^2 \rangle$ vs. $\langle \frac{\sin^2\theta}{\lambda^2} \rangle$ according to the relation

$$\log \left\langle \frac{F_o^2}{\Sigma f_o^2} \right\rangle = \log \frac{1}{k} - \frac{2B}{2.303} \left\langle \frac{\sin^2\theta}{\lambda^2} \right\rangle$$

derived by Wilson (1942). These were found to be $\frac{1}{8}\sqrt{k} = 12.2$

(for 1/8 of the unit cell) and B = 2.72 cm^2. The height of the Patterson origin peak was calculated by two approaches using these values of k and B. This led to the assignment of experimental peak heights to the interatomic vectors and to the conversion of the $F^2(000)$ term to the "floor" value.

In computing the Patterson synthesis it is customary to neglect the $F^2(000)$ term and the 8/V factor. Consequently, the relation between the theoretical and the experimental Patterson functions is expressed by

$$P_{theo}(XYZ) = \frac{8}{V} k P_{exp} + \frac{1}{V} F^2(000).$$

$F^2(000)$ can be calculated from the definition of a structure factor:

$$F(hk\ell) = \sum_{n=1} f_n \exp 2\pi i (hx_n+ky_n+\ell z_n),$$

so that

$$F^2(000) = \sum_{n=1} f_n^2 = [48(18+78)]^2 = 2.074 \times 10^7.$$

Since $V = 23.057 \cdot 15.040 \cdot 8.761$ Å $= 3038$ Å^3, $k = (8 \cdot 12.2)^2 = 9.5 \cdot 10^3$, and $P_{exp}(000) = 27{,}150$, the theoretical height of the origin peak is given by

$$P_{theo}(000) = \frac{8}{3038} \cdot 9.5 \cdot 10^3 \cdot 27{,}150 + \frac{1}{3038} \cdot 2.079 \cdot 10^7$$

$$= \underline{6.858 \cdot 10^5}.$$

The second approach, due to Atoji (1957), defines the height of the sharpened peak at the origin by

$$P(000) = \int_0^{s_0} 4\pi s^2 \frac{f_j(s)\ f_k(s)}{(\sum_i f_i / \sum_i z_i)^2} \exp\left(-\frac{B}{2} s^2\right) ds$$

where $s = (2 \sin\theta)/\lambda$, s_0 is the maximum value of s, f denotes the scattering factor, and z, the atomic number. By letting $f = \hat{f} \cdot z$ and $B/2 = g$ this expression simplifies to

$$P(000) = \sum_i z_i^2 \int_0^{s_0} 4\pi s^2 \left(-\frac{B}{2} s^2\right) ds$$

and is evaluated by letting $\int_0^{s_0} (\ ) = \int_0^{\infty} (\ ) - \int_{s_0}^{\infty} (\ )$ where the value of $\int_0^{\infty} (\ )$ is given in the standard integration tables and $\int_{s_0}^{\infty} (\ )$ is the Patterson termination error. Consequently

$$\int_0^{s_0} (\ ) = \frac{\pi}{g}^{3/2} - \frac{\pi}{g} \sqrt{\frac{\pi}{g}}\ \mathrm{erfc}\ (\sqrt{g} \cdot s_0) + 2s_0 \exp(-gs_0^2)$$

$$= \frac{\pi}{g}^{3/2} [1 - \mathrm{erfc}\ (\sqrt{g} \cdot s_0)] - \frac{\pi}{g} \cdot 2s_0 \exp(-gs_0^2)$$

Since $g = B/2 = 1.36$ and $s_0 = 2/1.542 = 1.30$,

$$\int_0^{s_0} (\ ) = 3.51\ \mathrm{erf}\ (1.516) - 6 \exp(-2.3) = 3.51 \cdot 0.968 - 6 \cdot 0.1 = 2.80$$

and

$$P(000) = 2.80 \cdot 48(18^2 + 78^2) = \underline{8.565 \cdot 10^5}.$$

The disagreement between the two results is due chiefly to the fact that the first considers only reflections which were actually recorded whereas the second refers to all

reflections. For the practical purpose of Patterson interpretation, the theoretical height of a sharpened peak is therefore given by

$$P_{theo}(XYZ) = \frac{6.86}{8.56} \; 2.8 \; z_i z_j = \frac{8}{V} k \; P_{exp} + \frac{1}{V} F^2(000)$$

and

$$P_{exp}(XYZ) = \frac{1}{250} (2.24 \; z_i z_j - 6843) = 0.009 \; z_i z_j - 27.4,$$

where 27.4 is the floor value. Thus experimental peak heights for single Bi-Bi, Bi-Cl, and Cl-Cl vectors are 27.4, -14.8, and -24.5 respectively.

Discovery of large peaks along the P(00Z) line section, indicative of atoms having the same x and y coordinates, gave first experimental proof of the presence of a mirror plane in the c direction. It further established a center of symmetry and confirmed the choice Pnnm as the correct space group. Subsequently, Okaya and Pepinsky* reported a negative piezoelectric test for BiCl which does not deny the center of symmetry. The absence of a peak at ½,½,½ excluded the existence of two-fold and four-fold sets except as listed in Figure 3.

Interpretation of the three-dimensional Patterson proved to be the turning point in the structure determination. All

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*Okaya, Y. and Pepinsky, R., Department of Chemistry, Pennsylvania State University, State College, Pennsylvania. Piezoelectric effect of BiCl. Private communication. 1960.

48 Bi positions were located by the same direct approach used for the two-dimensional case. This achievement practically solved the phase problem.

First, a list of all peaks was prepared specifying their position and height. Then, search for eight-fold Bi positions was begun by locating the positions of intraset vectors $0,0,\pm 2z$ in the P(X0Z) Patterson section shown in Figure 6, thereby establishing the allowed values of the z coordinate. Turning to the P(X½Z) section in Figure 7, peaks along the $z = \frac{1}{2}$ edge were taken to represent in part the intraset vectors $\frac{1}{2}\pm 2x,\frac{1}{2},\frac{1}{2}$ and used to obtain the x coordinates. The matching peaks at $\frac{1}{2}\pm 2x,\frac{1}{2},\frac{1}{2}\pm 2z$, which are required by eight-fold sets, specified one of the allowed z coordinates. The P(½YZ) section shown in Figure 8 served as the source of y coordinates. Here peaks along the $z = \frac{1}{2}$ edge and their counterparts with allowed z values were interpreted to represent the $\frac{1}{2},\frac{1}{2}\pm 2y,\frac{1}{2}$ and $\frac{1}{2},\frac{1}{2}\pm 2y,\frac{1}{2}\pm 2z$ intraset vectors, respectively. The intraset screening process was concluded by checking for the presence of $\pm 2x,\pm 2y,0$ and $\pm 2x,\pm 2y,\pm 2z$ vector peaks corresponding to the proposed combinations.

Search for four-fold sets followed the same general lines although vectors $\frac{1}{2}\pm 2x,\frac{1}{2},\frac{1}{2}\pm 2z$ and $\frac{1}{2},\frac{1}{2}\pm 2y,\frac{1}{2}\pm 2z$, and $\pm 2x,\pm 2y,\pm 2z$ were not allowed and the number of checks was reduced accordingly. In all cases, care was taken to observe height requirements corresponding to the multiplicities listed for each

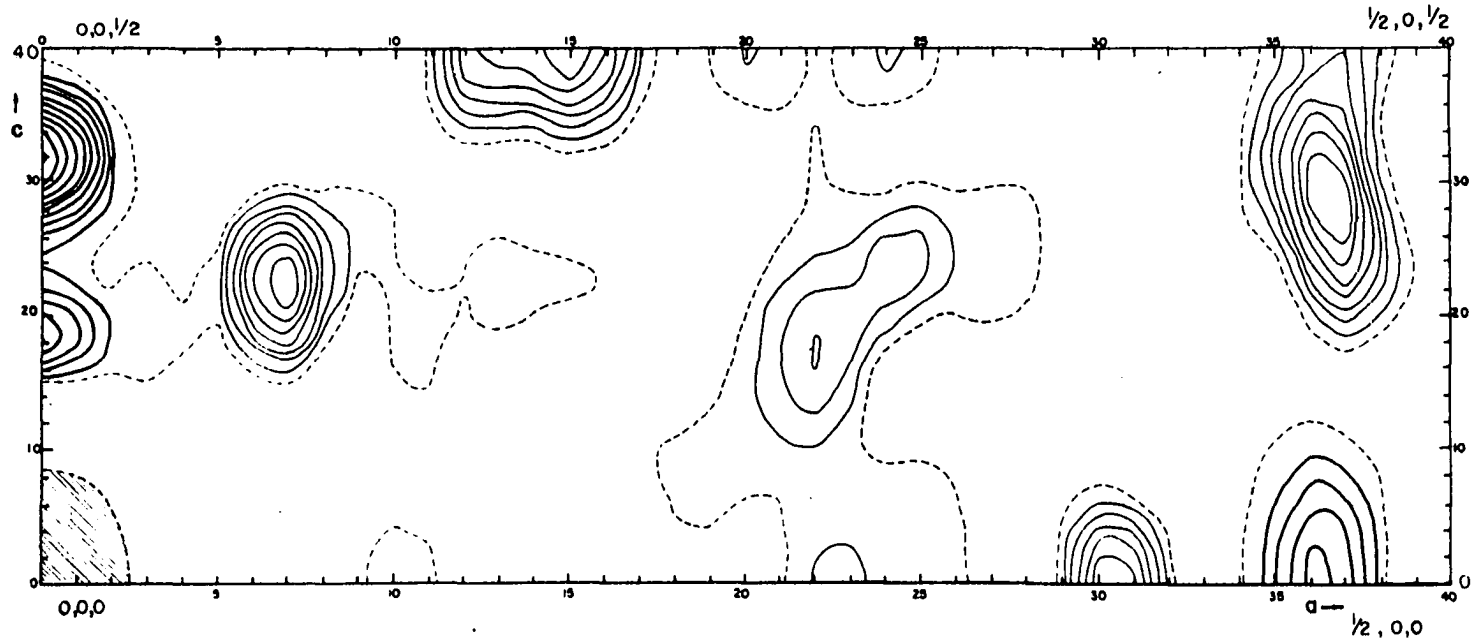

Figure 6. Sharpened Patterson section P(XOZ); thick contours are drawn at intervals corresponding to a Bi-Bi vector, thinner contours represent 2/5 of this value

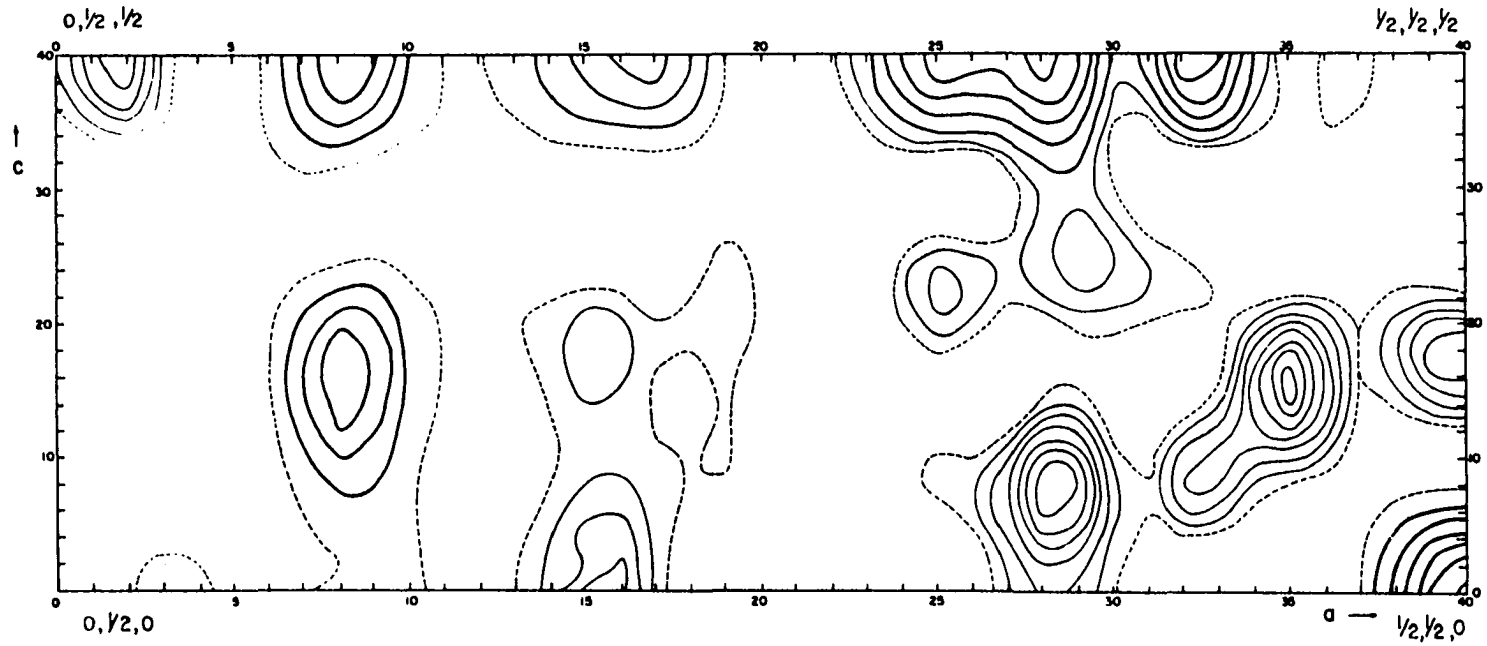

Figure 7. Sharpened Patterson section P(X½Z); thick contours are drawn at intervals corresponding to a Bi-Bi vector, thinner contours represent 2/5 of this value

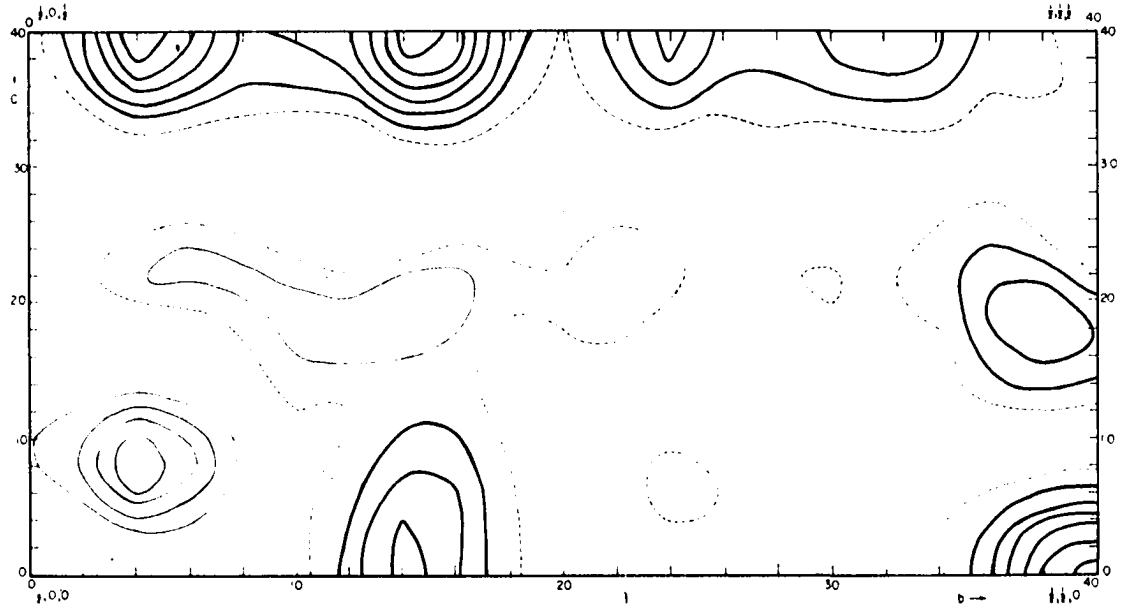

Figure 8. Sharpened Patterson section P(½YZ); thick contours are drawn at intervals corresponding to a Bi-Bi vector, thinner contours represent 2/5 of this value

vector in Table 2.

The characteristic Patterson ambiguity which was touched upon in dealing with the two-dimensional case was now compounded by the two sign possibilities for the z parameter. The choice of origin was again made arbitrarily by selecting a particular representation for one of the eight-fold sets and adopting this as reference for all the other newly-found sets.

In the second stage of interpretation, the Bi positions were further screened by inspection of the respective inter-set vectors which are listed in general form in Table 3. This criterion soon demonstrated its usefulness by proving that one of the three eight-fold Bi positions just acquired was not consistent with the other two. Eventually, two eight-fold and six four-fold sets were located for a total of 40 Bi positions.

The last eight positions played "hard to get" and a special ruse was devised to flush them out. It was reasoned that since there was good evidence for widespread Bi-Bi bonding, at least one atom of the new set or sets would generate a vector about 3 Å long with the cooperation of one other Bi atom. Close examination of all peaks at the indicated distance from the origin eventually led to the location of the final eight-fold set. All nine independent position were refined by hand to give the best possible over-all agreement with the position of Patterson peaks. Results are listed in

Table 4.

Calculation of Structure Factors

Structure factors are defined by the general expression:

$$F(hk\ell) = \sum_r f_r(hk\ell) \exp 2\pi i\ (hx_r + ky_r + \ell z_r)$$

$$= \sum_r f_r(hk\ell) \cos 2\pi(hx_r + ky_r + \ell z_r) + i \sin 2\pi(hx_r + ky_r + \ell z_r)$$

$$= A' + i\,B'$$

where f_r is the scattering factor and x_r, y_r, z_r, the coordinates of atom r. Since the structure has a center of symmetry, $F(hk\ell) = F(\bar{h}\bar{k}\bar{\ell})$, $A' + iB' = A'-iB'$, $B' = 0$ and the above relation reduces to

$$F(hk\ell) = \sum_r f_r(hk\ell) \cos 2\pi(hx_r + ky_r + \ell z_r)$$

Let $A = \sum_s \cos 2\pi(hx_s + ky_s + \ell z_s)$ where the summation applies to equivalent positions in the unit cell only. Then, substituting the general eight-fold positions from Figure 3,

$$A = 2\cos 2\pi(hx + ky + \ell z) + 2\cos 2\pi(-hx - ky + \ell z) + 2\cos 2\pi\left(hx - ky - \ell z + \frac{h + k + \ell}{2}\right) + 2\cos 2\pi\left(-hx + ky - \ell z - \frac{h + k + \ell}{2}\right)$$

which eventually reduces to

Table 4. Bi positions from Patterson analysis

No. of atom	Positions x	y	z
I	.047	.222	.199
II	.199	.157	.195
III	.412	.457	0
IV	.096	.072	0
V	.071	.399	0
VI	.414	.099	0
VII	.357	.189	½
VIII	.237	.330	0
IX	.152	.342	.277

$$A = \begin{cases} 8 \cos 2\pi hx \cos 2\pi ky \cos 2\pi \ell z & \text{for } h + k + \ell = 2n \\ -8 \sin 2\pi hx \sin 2\pi ky \cos 2\pi \ell z & \text{for } h + k + \ell = 2n + 1 \end{cases}$$

for eight-fold sets and half this quantity for four-fold sets. Thus, in its operational form, the structure factor is related to the atomic scattering factors by the equation

$$F(hk\ell) = \sum_t f_t(hk\ell) \cdot A_t(hk\ell) =$$

$$\begin{cases} 8 \sum_t f_t(hk\ell) \cos 2\pi hx_t \cos 2\pi ky_t \cos 2\pi \ell z_t \\ \qquad\qquad \text{for } h + k + \ell = 2n \\ -8 \sum_t f_t(hk\ell) \sin 2\pi hx_t \sin 2\pi ky_t \cos 2\pi \ell z_t \\ \qquad\qquad \text{for } h + k + \ell = 2n + 1 \end{cases}$$

where the summation applies only to independent atoms in the unit cell.

Atomic scattering factors for Bi^+ and Cl^- were obtained from Ibers*. The Bi^+ factors were based on the Thomas-Fermi-Dirac treatment and came from unpublished work by Thomas, King, and Umeda. The scattering factors for Cl^- were derived by Boys from an earlier paper by Boys and Price.

Before their introduction into structural calculations during the INCOR-IM computation stage, the Bi^+ scattering factors were corrected for anomalous dispersion (Templeton, 1955). Anomalous dispersion of x-ray radiation is due in part to the reduced scattering power of the shielded, inner electrons and, in part, to the interaction of the incident radiation with the characteristic frequency of the scattering electrons. The corrected scattering factor is related to the original scattering factor, f_o and to the real and imaginary corrections, $\Delta f'$ and $\Delta f''$ by the equation

$$f = f_o + \Delta f' + i\,\Delta f''.$$

Because of the difficulty inherent in handling the imaginary correction it is customary to calculate the absolute magnitude of the corrected scattering factor according to the equation

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*Ibers, J. H., Shell Development Company, Emeryville, California. Form factors for Bi, Bi^+, and Cl^-. Private communication. 1959.

$$f = \sqrt{(f_o + \Delta f')^2 + (\Delta f'')^2} \cong f_o + \Delta f' + \tfrac{1}{2} \frac{(\Delta f'')^2}{f_o + \Delta f'}$$

The values of $\Delta f'$ and $\Delta f''$ reported by Dauben and Templeton (1955) for Bi atoms and the Cu Kα radiation are -5 and 9, respectively. The anomalous dispersion correction was ultimately applied by subtracting 5 from scattering factors at all angles. It was felt that the uncertainty in the charge of the Bi species and the controversy surrounding the anomalous dispersion theory did not warrant the inconvenience of computing the relatively small, second correction term. The correction for Cl atoms is quite negligible and was omitted.

The actual computation of structure factors was performed on the I.B.M. 650 computer using the LS-IIM2 least squares program, and expanded version of LS-II (Senko et al., 1957), which was modified to calculate structure factors only. This modification is designed to reduce the computing time by omitting certain portions of the least squares calculations. Atomic parameters from the three-dimensional Patterson were fed into the program along with the 1938 observed reflections, the scattering factors, the absolute over-all scale factor, and the average temperature factor. The output included observed and calculated structure factors and, for each layer, optimum scale factors, and R_3 residuals. A list of the ob-

served and calculated structure factors for the final structure is given in Appendix B.

Electron Density Maps

With most structure factor signs correctly assigned on the basis of the strongly-diffracting Bi atoms, attention was turned to the computation of electron density maps and the search for Cl positions.

The general expression for the electron density in a crystal is

$$\rho(XYZ) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{l=-\infty}^{\infty} F(hkl) \exp\left[-2\pi i(hX+kY+lZ)\right]$$

where X, Y, and Z indicate grid points rather than atomic coordinates. As with the Patterson function, the expression for centrosymmetric structures reduces to

$$\rho(XYZ) = \frac{8}{V} \sum_{h} \sum_{k} \sum_{l=0}^{\infty} F(hkl) \cos 2\pi hX \cos 2\pi kY \cos 2\pi lZ \quad \text{for } h + k + l = 2n$$

$$- \frac{8}{V} \sum_{h} \sum_{k} \sum_{l=0}^{\infty} F(hkl) \sin 2\pi hX \sin 2\pi kY \cos 2\pi lZ \quad \text{for } h + k + l = 2n + 1$$

or, more specifically, to

$$\rho(XYZ) = \frac{1}{V} F(000) + \frac{2}{V}\left[\sum_{h} F(h00) \cos 2\pi hX + \sum_{k} F(0k0) \cos 2\pi kY + \sum_{l} F(00l) \cos 2\pi lZ\right] + \frac{4}{V}\left[\sum_{h} \sum_{k} F(hk0) \cos 2\pi hX \cos 2\pi kY + \sum_{h} \sum_{l} F(h0l) \cos 2\pi hX \cos 2\pi lZ\right]$$

(Continued next page)

$$+ \sum_h \sum_l F(0k\ell) \cos 2\pi kY \cos 2\pi \ell Z \,]$$

$$+ \frac{8}{V} \sum_h \sum_k \sum_\ell F(hk\ell) \cos 2\pi hX \cos 2\pi kY \cos 2\pi \ell Z, \text{ for } h+k+\ell=2n$$

$$\rho(XYZ) = -\frac{2}{V} [\sum_h F(h00) \sin 2\pi hX + \sum_k F(0k0) \sin 2\pi kY$$

$$+ \sum_\ell F(00\ell) \cos 2\pi \ell Z] - \frac{4}{V}[\sum_h \sum_k F(hk0) \sin 2\pi hX \sin 2\pi kY$$

$$+ \sum_h \sum_\ell F(h0\ell) \sin 2\pi hX \cos 2\pi \ell Z + \sum_k \sum_\ell F(0k\ell) \sin 2\pi kY \cos 2\pi \ell Z]$$

$$- \frac{8}{V} \sum_h \sum_k \sum_\ell F(hk\ell) \sin 2\pi hX \sin 2\pi kY \cos 2\pi \ell Z,$$

$$\text{for } h + k + \ell = 2n + 1$$

Structure factors for special reflections were divided by their appropriate multiplicity factors in accordance with the above relations and the summing codes specifying the evenness or oddness of indices and the form of the electron density expression were supplied for each reflection. All unobserved reflections and those with $F_o \gg F_c$ were excluded. The summation was performed on an 1/80 x 1/80 x 1/40 grid with the aid of the I.B.M. 650 computer and the TDF-2 program. Results were again compiled on the I.B.M. 407 tabulator equipped with the special wiring panel. Contours were plotted in the conventional manner. Beside the nine original Bi

positions, 21 other peaks appeared. These are all listed in Table 5.

Table 5. Atomic positions from Fourier analysis

No. of atom	Positions x	y	z
X	0	0	.290
I	.045	.222	.196
	.045	.224	.290
XI	.045	.425	½
V	.071	.399	0
	.072	.398	.232
IV	.095	.070	0
	.095	.069	.232
XII	.111	.132	½
XIII	.262	.288	½
XIV	.290	.054	½
XV	.314	.017	0
XVI	.334	.210	.192
XVII	.334	.443	.209
	.354	.193	.266
VII	.358	.191	½
	.380	.272	0
	.409	.459	.232

Interpretation of all 21 peaks as indicative of Cl positions would have resulted in a total of 128 Cl atoms per unit cell in drastic violation of Corbett's chemical analysis. Furthermore, some of the alleged locations were closer to Bi atoms than was allowed by legitimate bond distances. Several devices, including least squares cycles on very limited samples and two-dimensional difference Fourier projections, were used in a vain effort to cope with this excess. Finally, it became evident that more fundamental measures were called for. Some of the extra peaks were thought to have been contributed by reinforced ripples caused by the series termination effects of nearby Bi atoms. A three-dimensional difference Fourier which is free of this defect was expected to save the day.

The difference Fourier, more properly known as the error synthesis, provides a direct portrayal of the discrepancy between the structure represented by the observed intensities and the postulated model. Strongly negative regions in the contour maps indicate that too much scattering matter has been assumed there, while positive regions indicate that too little matter has been assigned. A steep negative gradient at an assumed atomic position implies that the atom is slightly out of place and should be moved toward the nearest positive area. The error synthesis is computed in the same manner as the more conventional Fourier synthesis except that

the signed differences F_o-F_c are used as Fourier coefficients, rather than the observed structure factors with calculated signs.

In order to render the results more meaningful, the original Bi positions and the corresponding temperature factors were partially refined by running 250 reflections, selected more or less at random, through two cycles of the LS-IIM2, least squares program. The results, listed in Table 6, were then used to compute structure factors for the difference Fourier. Contrary to past practice, all operations preliminary to the summation were handled on the I.B.M. 650 computer by means of the new TDF-2 COEFFICIENT program (Stucky, 1960). These operations comprised the elimination of reflections which were unobserved or smaller than a given minimum and reflections with $F_o/F_c > 3$. They also included the division of special reflections by their respective multiplicity factors, the provision of the proper electron density form and summation codes, and the selection of the signed differences F_o-F_c as Fourier coefficients. The summation was carried out in the conventional manner on an 1/80 x 1/80 x 1/40 grid. The output was tabulated and printed directly on a grid-form from which 11 positive and nine negative peaks were read off by inspection. These are reported in Table 7.

The positive peaks, interpreted as Cl positions,

Table 6. Bi parameters refined by LS-IIM2

Atom no.	Position			B	Layer no.	K	R_3
I	.0463	.2234	.1956	2.02	0	12.68	.0520
II	.1992	.1552	.1870	2.19	1	11.68	.0843
III	.4100	.4570	0	1.44	2	13.74	.0803
IV	.0980	.0698	0	2.08	3	11.50	.0481
V	.0709	.3970	0	2.50	4	10.67	.1173
VI	.4125	.1004	0	2.61	5	12.52	.0579
VII	.3579	.1897	½	1.58	all		.0657
VIII	.2373	.3284	0	2.01	all (R_1)		.2442
IX	.1534	.3431	.2710				

Table 7. Atomic positions from three-dimensional difference Fourier

Atom no.	Position			Atom no.	Position		
I	.048	.222	.190	XI	.048	.419	½
II	.199	.155	.187	XII	.109	.130	½
III	.411	.456	0	XIII	.261	.286	½
IV	.099	.071	0	XIV	.291	.054	½
V	.071	.397	0	XV	.316	.015	0
VI	.414	.102	0	XVI	.334	.216	.191
VII	.357	.194	½	XVII	.333	.441	.209
VIII	.240	.330	0	XVIII	.433	.329	½
IX	.152	.341	.269	XIX	.445	.085	.296
X	0	0	.290	XX	.466	.280	0

generated 56 Cl atoms per unit cell, eight more than the number of Bi atoms. These peaks were all part of the group evolved from the three-dimensional Fourier synthesis but their defiance of the 1:1 stoichiometry was less brazen and almost tolerable. The negative peaks were indicative only of anisotropic thermal motion or minor positional shifts for certain Bi atoms.

A drawing of the unit cell, complete with the locations of all atoms found thus far, presented an arrangement which was very plausible, though admittedly unorthodox. Agreement between observed and calculated structure factors was very good for this stage of structure determination and the Bi-Bi vectors checked well with Patterson peaks. It was therefore felt that this model was essentially correct and that the time had come to proclaim victory of mind over matter and to settle down to the lesser tasks of refining the atomic coordinates and temperature factors, calculating interatomic distances and angles, and exercising every legitimate effort to relieve the structure of eight embarrassing Cl atoms.

STRUCTURE REFINEMENT AND FUNCTIONAL ANALYSIS

The process of structure refinement was assigned the dual purpose of pinpointing the atomic coordinates in order that the type of species formed by successive bond ruptures could be identified correctly and of assessing the general accuracy of the proposed model including the eight uncooperative Cl atoms. The functional analysis computation provided bond distances and angles along with their standard deviations.

Refinement of Structure

The structure was refined by the method of least squares. The advantages of this approach lie in the elimination of the series termination error and the provision of a means to regulate the influence of a reflection in such a manner that its contribution be commensurate with the accuracy of the original intensity measurement. The theory of error predicts that, if the errors of observed structure factors follow the Gaussian distribution, then the best atomic parameters will be those which result in the minimization of the residual

$$R = \sum_i [\sqrt{w_i}\ (|F_o| - |F_c|)_i]^2,$$

where w is a weighting factor. This is the fundamental concept of least squares refinement.

The two programs available for least squares computations

were the LS-IIM2, used previously for calculation of structure factors, and a program by Busing and Levy (1959a) written for the I.B.M. 704 computer. Due to the space and speed limitations of the I.B.M. 650, the LS-IIM2 program solves the system of normal equations on the basis of a diagonal approximation to the full matrix. It was estimated that the Busing and Levy program would be three times more effective and 20 times faster than the "650" program. Five least squares cycles with isotropic temperature factors were run on the I.B.M. 704 computer at the Midwest Universities Research Association in Madison, Wisconsin. The structure refined very satisfactorily lowering the residual

$$R_1 = \frac{\Sigma \left| |F_o| - |F_c| \right|}{\Sigma |F_o|}$$

from an initial value of about 0.26 to 0.156. The output of cycle 5 is given in Table 8. Figure 9 shows a drawing of the complete structure, projected on the (001) plane.

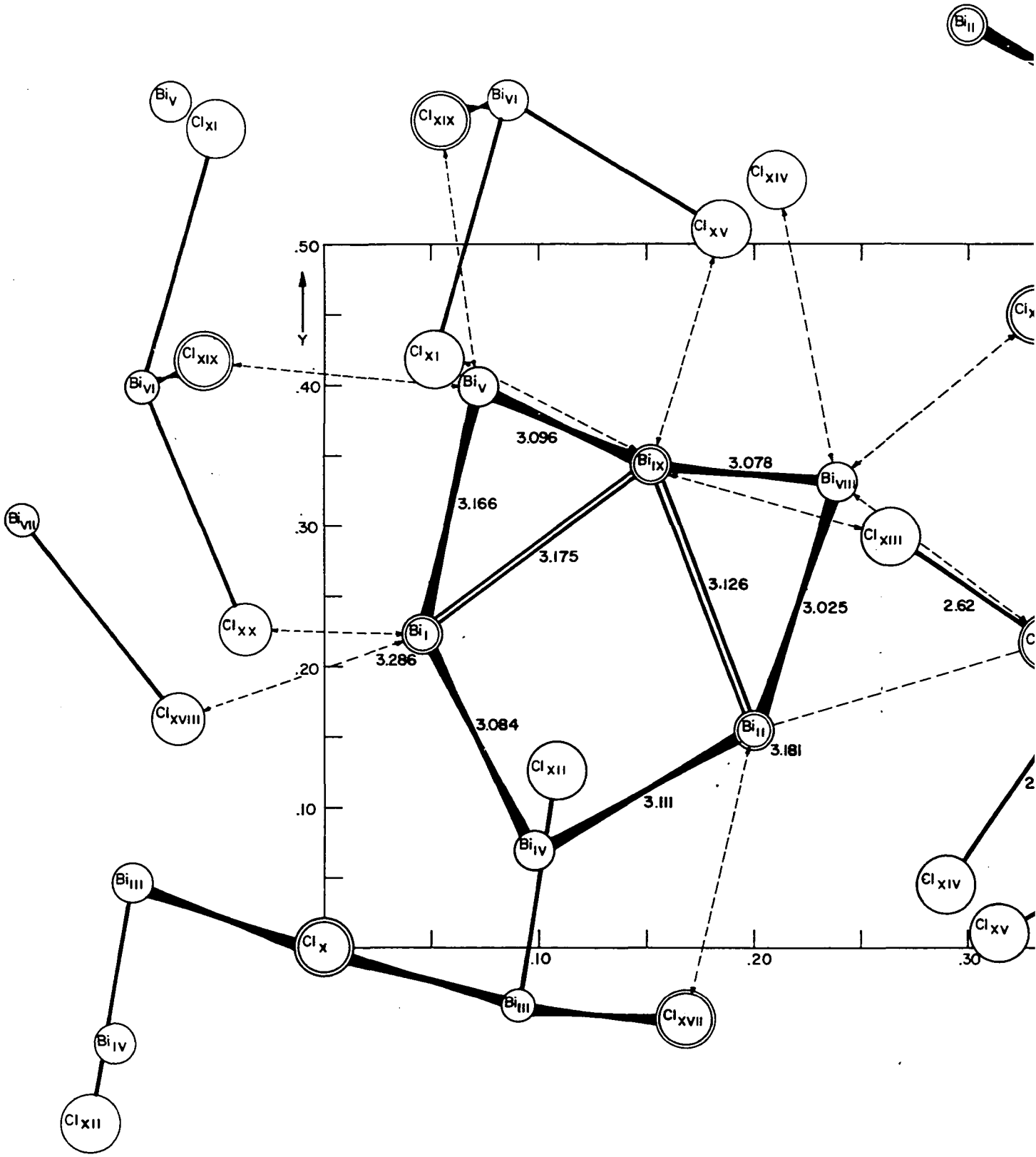
Throughout the refinement no grounds appeared for dismissing any of the Cl positions. As a further check of their validity, a three-dimensional difference Fourier was computed on the basis of the refined parameters following the operational procedure described previously. The lack of negative peaks at the assigned Cl positions confirmed their authenticity and precluded the possibility of disordered Cl atoms.

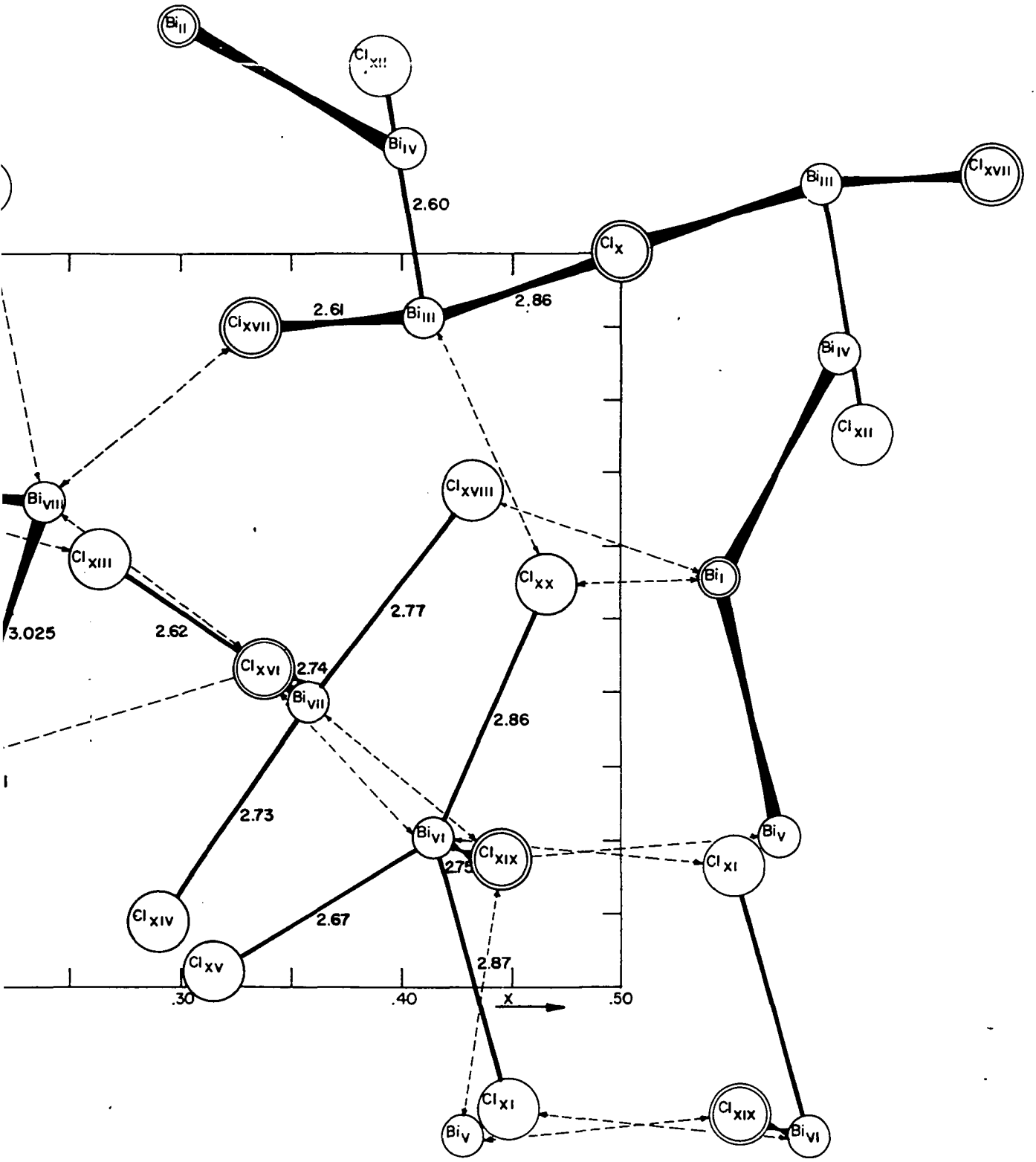
Table 8. Atomic parameters after final refinement

Atom no.	Positions						B
I	.0459	±.0002	.2229	±.0003	.1876	±.0007	3.25 ± .07
II	.2002	±.0002	.1544	±.0002	.1815	±.0006	2.96 ± .07
III	.4101	±.0002	.4550	±.0003	0		2.07 ± .07
IV	.0984	±.0002	.0692	±.0003	0		2.52 ± .07
V	.0723	±.0003	.3982	±.0004	0		3.70 ± .10
VI	.4139	±.0002	.1009	±.0004	0		3.39 ± .10
VII	.3578	±.0002	.1930	±.0002	½		1.75 ± .06
VIII	.2390	±.0002	.3296	±.0003	0		2.25 ± .07
IX	.1525	±.0002	.3425	±.0003	.2669	±.0007	3.43 ± .08
X	0		0		.288	±.005	2.3 ± .4
XI	.052	±.001	.418	±.002	½		3.1 ± .5
XII	.109	±.001	.126	±.002	½		2.6 ± .4
XIII	.264	±.002	.291	±.003	½		5.0 ± .8
XIV	.290	±.001	.044	±.002	½		3.6 ± .5
XV	.315	±.001	.010	±.002	0		3.5 ± .5
XVI	.338	±.001	.216	±.002	.194	±.004	3.4 ± .4
XVII	.332	±.001	.449	±.002	.216	±.004	3.4 ± .4
XVIII	.433	±.001	.337	±.001	½		1.8 ± .3
XIX	.445	±.001	.086	±.002	.302	±.005	4.5 ± .5
XX	.466	±.001	.274	±.001	0		1.2 ± .3

K_0 = 12.72, K_2 = 13.50, K_4 = 12.71, R_3 = .187
K_1 = 12.00, K_3 = 12.34, K_5 = 13.20, R_1 = .156

Figure 9. Structure of BiCl projected onto the (001) plane


Bi V
Cl XI
Cl XIX
Bi VI
Cl XV
Cl XIV
Bi II
.50
Y
.40
.30
.20
.10
Cl XI
Bi V
3.096
Bi IX
3.078
Bi VIII
3.166
3.175
3.126
3.025
Cl XIII
2.62
Bi VII
Cl XX
Bi I
3.286
3.084
Cl XVIII
Bi II
3.181
Cl XII
3.111
Bi IV
Bi III
Cl X
.10
.20
.30
Cl XVII
Bi IV
Cl XII
Cl XIV
Cl XV


Bi II
Cl XII
Bi IV
2.60
Cl XVII
2.61
Bi III
2.86
Cl X
Bi III
Cl XVII
Bi IV
Cl XII
Bi VIII
Cl XVIII
Cl XIII
Cl XX
Bi I
3.025
2.62
2.77
Cl XVI
2.74
Bi VII
2.86
2.73
Bi VI
Cl XIX
Bi V
Cl XI
2.75
Cl XIV
2.67
Cl XV
2.87
.30
.40
X
.50
Cl XI
Cl XIX
Bi V
Bi VI

Finally, a two-dimensional difference Fourier projection onto the (001) plane, based on the refined Bi parameters alone, produced Cl peaks with the expected height ratios. This served to dispel once again the disorder specter and, even more important, to confirm the presence of eight-fold Cl positions.

The three-dimensional difference Fourier allowed a glance at the anisotropic thermal motion of Bi atoms. Figure 10 shows the positions of anisotropic peaks in relation to Bi atoms. Relative peak heights are given in parentheses; the average height of a Bi peak would be about 450 on the same scale.

Weighting of Intensities

The weighting of individual reflections has been discussed briefly by Lipson and Cochran (1957, pp. 281 and 282). The weighting factor is inversely proportional to the square of an estimated standard deviation of the observed intensity, i.e., $w = 1/\sigma^2(I_o)$. The underlying concept is that the contribution of each reflection to the residual be commensurate with the accuracy assigned to the original observation.

The most valid criterion for the accuracy of an observed intensity is the number of films which contribute to its experimental evaluation. In addition, it is customary to penalize very weak reflections because of their sensitivity

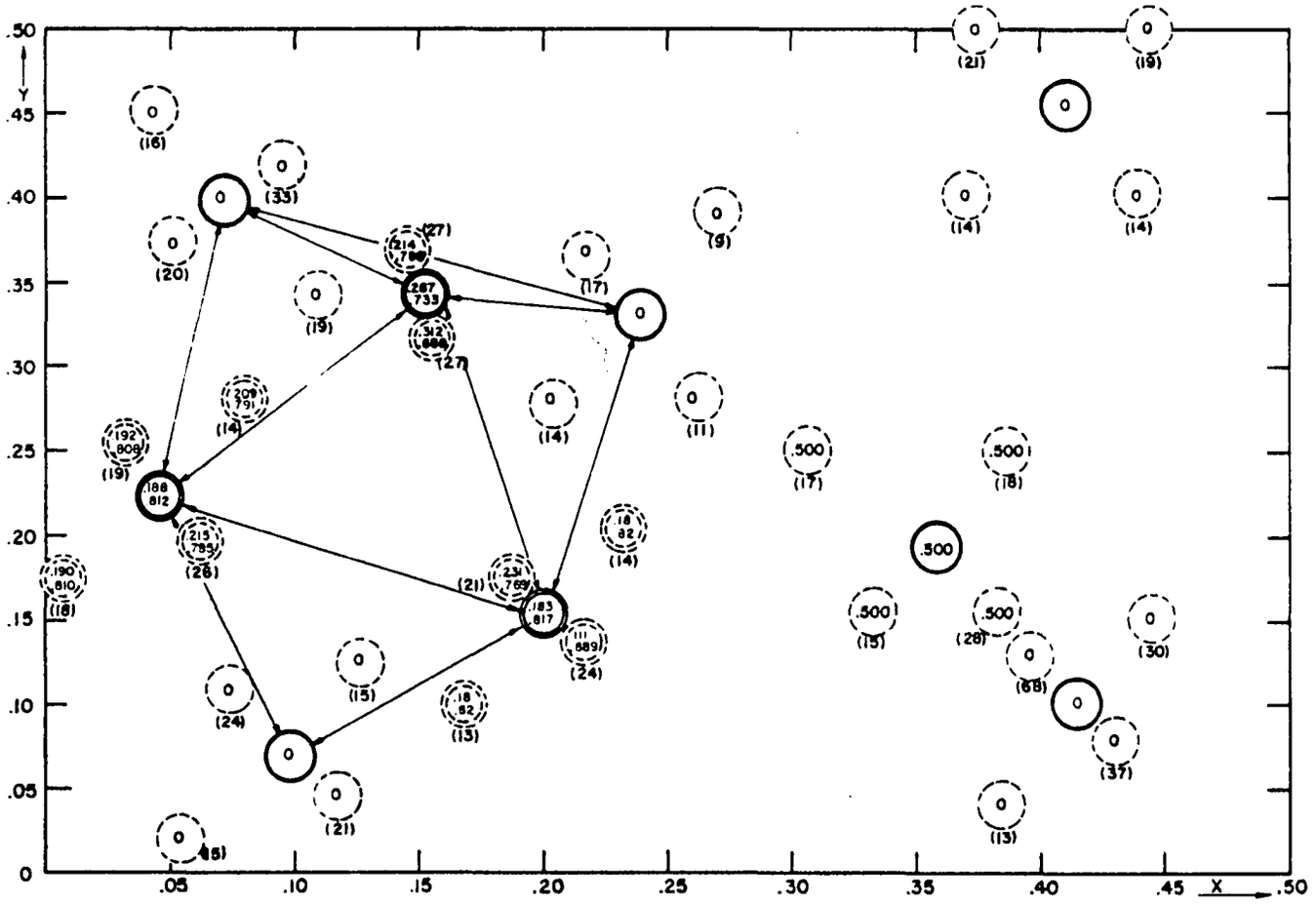


Figure 10. Anisotropic thermal motion of Bi atoms

to minute variations in the film background. For each set of Weissenberg intensities there exists a quantity I_m, the lowest observable intensity, and a quantity I_b, the midpoint of the best judged range. I_b is often equal to 16 I_m.

Reflections with $I_o \geq I_b$ fell generally within the judgeable range on the maximum number of films (3). Their relative error was therefore assumed constant and estimated at 10% on the basis of the observed precision. Mathematically this condition is expressed by

$$\frac{\sigma(I_o)}{I_o} = 0.1$$

For reflections with $I_o < I_b$, the relative error should rise gently at first for decreasing intensities, as the number of contributing films drops to two, then, more rapidly, as only one film becomes available and background variations gain in importance. The relation

$$\frac{\sigma(I_o)}{I_o} = 0.1 \left(\frac{I_b}{I_o}\right)^{3/4}$$

was found to satisfy the statistical formula for the change in standard deviation with decreasing number of observations and to coincide with a reasonable estimate for the error of I_m.

The contribution of errors in the Lorentz, polarization, and absorption corrections to the standard deviations of corrected intensities was calculated by means of the formula for the propagation of error. If

$$I_{corr} = I_{uncorr} \cdot X_{LPA},$$

where X_{LPA} is the product of the Lorentz, polarization, and absorption correction, then

$$(I_{corr}) = \left\{\sigma^2(X)\left[\frac{\partial(I_{corr})}{\partial X}\right]^2 + \sigma^2(I_{uncorr})\left[\frac{\partial(I_{corr})}{\partial(I_{uncorr})}\right]^2\right\}^{\frac{1}{2}}$$

$$= \left\{\sigma^2(X)\ I_{uncorr}^2 + \sigma^2(I_{uncorr})\cdot X^2\right\}^{\frac{1}{2}}$$

Assuming only experimental error and neglecting any inaccuracies inherent in the theoretical treatment of these corrections, it was found that

$$\left[\frac{\sigma(X)}{X}\right]^2 << \left[\frac{\sigma(I_{uncorr})}{I_{uncorr}}\right]^2$$

This reduced the above expression to

$$\sigma(I_{corr}) \cong \sigma(I_{uncorr})\cdot X$$

or

$$\frac{\sigma(I_{corr})}{I_{corr}} \cong \frac{\sigma(I_{uncorr})}{I_{corr}}\cdot X = \frac{\sigma(I_{uncorr})}{I_{uncorr}}$$

The Busing and Levy least squares program requires for each reflection the standard deviation of the structure factor. It can be shown that this quantity is related to the standard deviation of the observed intensity by the equation

$$\sigma(F_o) = \tfrac{1}{2}\ \frac{\sigma(I_{corr})}{I_{corr}}\ F_o \cong \tfrac{1}{2}\ \frac{\sigma(I_o)}{I_o}\ F_o$$

Substituting in the earlier expressions for $\sigma(I_o)$, the working formulation of $\sigma(F_o)$ becomes

$$\sigma(F_o) = \begin{cases} .05\ F_o & \text{for } I_o \geq I_b \\ .05\left(\frac{I_b}{I_o}\right)^{3/4} F_o & \text{for } I_o < I_b \end{cases}$$

A new program, identified as "STD", was written for the I.B.M. 650 computer for the purpose of computing standard deviations of structure factors on the basis of uncorrected intensities. A detailed writeup will be found in Appendix A.

Figure 11 compares a graphic representation of this treatment with corresponding plots based on a scheme by Williams and Fitzwater as incorporated in the LS-IIM2 program. The major faults of the latter approach lie in its failure to base calculation of standard deviations on the uncorrected intensities and in the inordinately sharp rise of $\sigma(F_o)$ for weak reflections. This causes incorrect assignment of error estimates and the virtual elimination of contributions from very weak reflections.

Neither treatment considered the weighting of unobserved reflections. A detailed discussion of this problem has been presented by Hamilton (1955).

Functional Analysis

Interatomic distances and angles, along with their respective standard deviations, were computed by Dr. Lawrence Dahl at M.U.R.A. with the aid of the Crystallographic Function and Error program (Busing and Levy, 1959b). These are listed in Tables 9 and 10. Bonding distances are indicated in Figure 9.

Table 9. Interatomic distances in Å

Atom No.	Distance	Atom No.	Distance
I-I	3.286 ± .012	VII-XIII	2.617 ± .050
I-II	3.704 ± .005	VII-XIV	2.730 ± .034
I-IV	3.084 ± .006	VII-XVI	2.743 ± .037
I-V	3.166 ± .007	VII-XVIII	2.775 ± .021
I-IX	3.125 ± .006	VII-XIX	3.100 ± .037
I-X	3.625 ± .011		
I-XII	3.424 ± .017	VIII-IX	3.078 ± .006
I-XVIII	3.215 ± .018	VIII-XIV	3.296 ± .034
I-XIX	3.700 ± .032	VIII-XVI	3.311 ± .029
I-XX	3.297 ± .011	VIII-XVII	3.378 ± .028
II-II	3.181 ± .011	IX-XI	3.297 ± .024
II-IV	3.111 ± .006	IX-XII	3.977 ± .023
II-VIII	3.205 ± .005	IX-XIII	3.373 ± .040
II-IX	3.126 ± .006		
II-XII	3.525 ± .017	X-XII	3.64 ± .03
II-XIII	3.763 ± .034	X-XVII	3.94 ± .02
II-XIV	3.850 ± .024	X-XVIII	3.84 ± .03
II-XV	3.771 ± .031	X-XX	3.95 ± .02
II-XVI	3.305 ± .025		
II-XVII	3.306 ± .025	XI-XI	3.43 ± .06
		XI-XV	3.38 ± .05
III-X	2.860 ± .028	XI-XIX	3.62 ± .05
III-XII	2.605 ± .027	XI-XIX	3.67 ± .05
III-XVII	2.606 ± .032	XI-XX	3.48 ± .03
III-XX	3.017 ± .018		
		XII-XVII	3.54 ± .04
IV-X	3.553 ± .030	XII-XX	3.61 ± .03
IV-XVII	3.470 ± .031		
IV-XVIII	3.557 ± .021	XIII-XIV	3.76 ± .06
		XIII-XVI	3.36 ± .05
V-VIII	3.979 ± .007	XIII-XVII	3.79 ± .05
V-IX	3.096 ± .007	XIII-XVIII	3.95 ± .05
V-XIV	3.859 ± .035		
V-XIX	3.418 ± .037	XIV-XVI	3.89 ± .04
V-XIX	3.337 ± .036	XIV-XVII	3.68 ± .04
		XV-XVI	3.58 ± .04
VI-XI	3.185 ± .031		
VI-XI	2.870 ± .031	XVI-XVI	3.40 ± .08
VI-XV	2.666 ± .035	XVI-XVII	3.50 ± .03
VI-XVI	3.000 ± .030	XVI-XVIII	3.91 ± .03
VI-XIX	2.753 ± .046	XVI-XIX	3.29 ± .04
VI-XX	2.865 ± .018	XVI-XX	3.53 ± .03

Table 9. (Continued)

Atom No.	Distance	Atom No.	Distance
XVII-XVII	3.78 ± .07	XIX-XIX	3.46 ± .09
XVII-XVIII	3.79 ± .03	XIX-XIX	3.63 ± .06
		XIX-XX	3.90 ± .04

Table 10. Interatomic angles; central atom is vertex

Atom No.	Angle	Atom No.	Angle
I - I -V	58.7 ± .1	XV-VI -XX	145.8 ± .9
II - I -V	92.3 ± .2	XIX-VI -XIX	148.5 ± 1.4
I -II -VIII	92.7 ± .1	XIII-VII-XIV	89.3 ± 1.3
X -III-X	80.7 ± 1.3	XIII-VII-XVI	77.7 ± .6
X -III-XII	83.5 ± .5	XIII-VII-XVIII	94.2 ± 1.2
X -III-XVII	92.2 ± .9	XIV-VII-XVIII	176.5 ± .8
XII-III-XVII	85.4 ± .7	XVI-VII-XVI	155.4 ± 1.1
XVII-III-XVII	92.8 ± 1.3	II-VIII-V	86.8 ± .1
I -IV -II	73.4 ± .1	I-IV -VIII	107.7 ± .2
I -IV -II	105.1 ± .2	II-IX -V	105.9 ± .2
I -V -I	37.9 ± .1	V-IX -VIII	80.2 ± .2
I -V -VIII	88.3 ± .2	XVI-XIV-XVI	87.2 ± 1.2
XI -VI -XV	75.2 ± 1.0	XIV-XVI-XVIII	89.8 ± .9
XI -VI -XIX	81.4 ± .7	XVI-XVIII-XVI	86.5 ± 1.0
XI -VI -XX	139.0 ± .7		

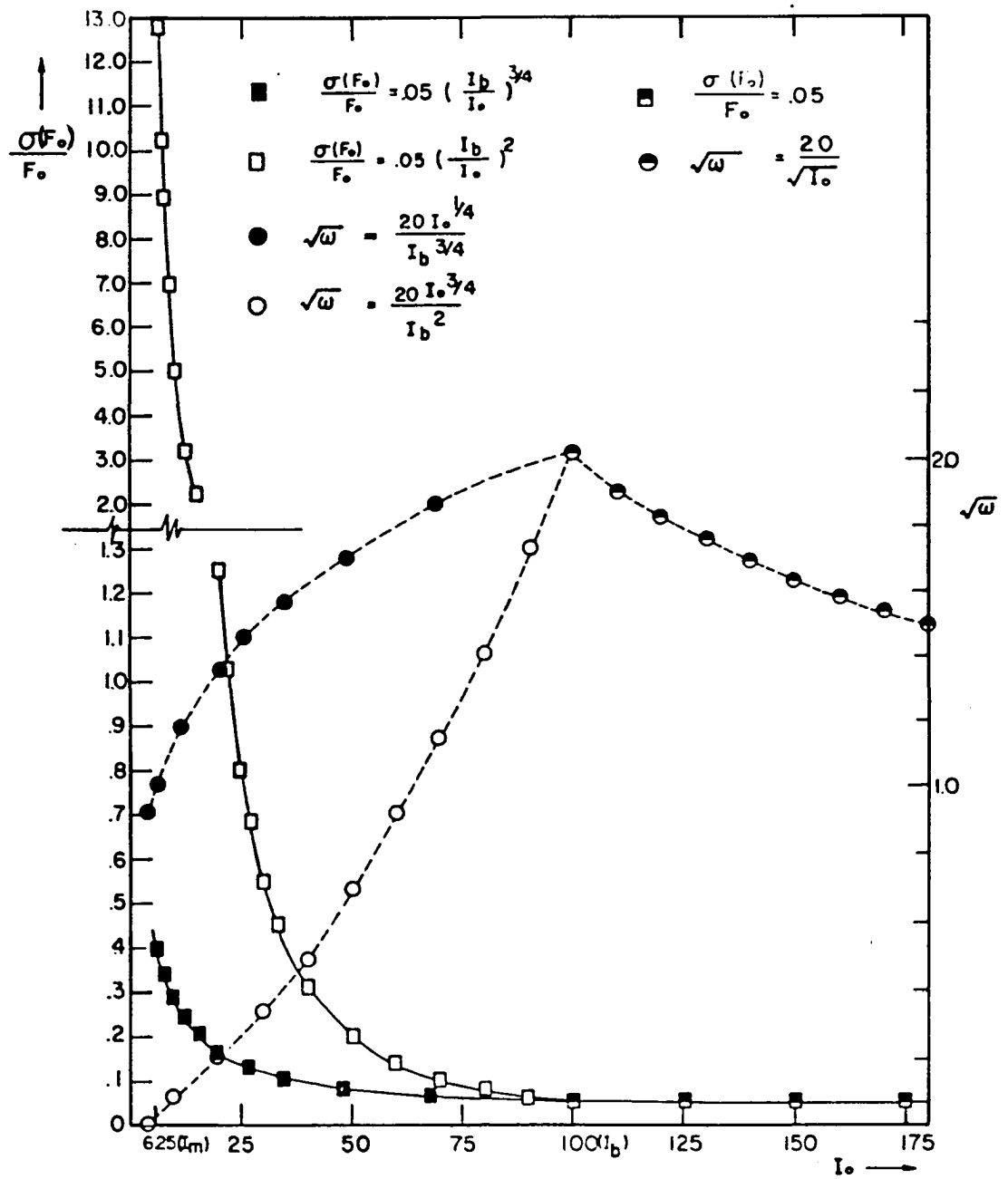


Figure 11. Standard deviation plots; full circles indicate the new approach

DISCUSSION

Interpretation of Structure

The unit cell of bismuth monochloride contains four Bi_9 polyhedra and an array of Bi and Cl atoms which can be catalogued as eight $BiCl_5$ and two Bi_2Cl_8 units. The Bi_9 polyhedron assumes the form of a distorted trigonal prism with atoms Bi_{IV} and Bi_{IX} (2) projecting from its faces. In $BiCl_5$ the Cl atoms form a distorted tetragonal pyramid about Bi; in Bi_2Cl_8 two such pyramids share an edge. Weak Bi-Cl interactions form the only links between molecules. Those shorter than 3.5 Å are indicated by dashed lines in Figure 9.

Each atom in the Bi_9 unit has four nearest neighbors at 3.08 Å to 3.29 Å. The shorter distance is the same as that between Bi and its three nearest neighbors in solid bismuth, the longer is comparable to the 3.32 Å distance in liquid bismuth. The elongation of Bi-Bi bonds and the concomitant distortion of the trigonal prism is induced by intermolecular Bi-Cl interactions whose average length of 3.3 Å is very close to the sum of the estimated Bi^+ and Cl^- ionic radii.

The effective radius, r, of an atom in a crystal lattice can be calculated by Pauling's (Pauling and Pauling, 1956) formula

$$r = r_1 - 0.300 \log_{10} \frac{v}{n}$$

from its simple covalent radius, r_1, its valence, v, and the

number of bonds it forms, n. For a Bi atom bonded to four neighbors, r_1 = 1.510, n = 4 and the simplified expression becomes

$$r = 1.510 - 0.300 \log_{10} \frac{v}{4} .$$

On this basis, a valence of 2 corresponds to an effective bond length of 3.20 Å, a valence of 3, to 3.09 Å, and a valence of 4, to the single covalent bond length of 3.02 Å. Since the distortion of the trigonal prism involves considerable stretching of most bonds and only slight compression of a few, the valence of 2 is incompatible with the average experimental bond length of 3.14 Å. The two other values are acceptable at this stage as they call for bonds which are either equal to or smaller than the shortest experimental distance, 3.08 Å.

The valence of 3 would place no charge on the Bi atom; the three bonding p electrons could distribute themselves among four metallic orbitals, each equivalent to 3/4 of an atomic orbital in accordance with Pauling's findings, and an inert s pair would be left to take up the void opposite from the center of the Bi_9 unit. However, such a disposition is incompatible with the diamagnetic character of the crystals as it calls for an odd number of electrons in the polyhedron. The valence of 4 requires a +1 charge on each Bi atom and, presumably, entails the distribution of two s and two p electrons among four highly distorted sp^3 orbitals. The happiest solution, however, stems from a molecular orbital approach

which can justify an intermediate valence and hence an intermediate net charge. Under these circumstances the pyramidal molecules can be regarded as $BiCl_5^=$ and $Bi_2Cl_8^=$ ions containing bismuth in its conventional Bi(III) state and Bi_9 is assigned a charge of +5 to insure charge conservation.

Bi-Cl bond lengths within the pyramidal molecules range between 2.60 and 2.87 Å. They are comparable to the Bi-Cl distance of 2.71 Å in BiSCl and BiSeCl but longer than the 2.48 Å distance in gaseous $BiCl_3$. Calculations based on the electronegativities of the two elements assign 25% ionic character to the Bi-Cl bond, but the distance in gaseous $BiCl_3$ is equal to the sum of covalent radii. The most perplexing aspect of bonding in the $BiCl_5^=$ and $Bi_2Cl_8^=$ ions is the role of the bridging intermolecular links between their Bi and Cl atoms which in this case are only 3.1 Å long. If these are counted along with the regular Bi-Cl bonds, atoms Bi_{III}, Bi_{VI}, and Bi_{VII} attain a sixfold, sevenfold, and even eightfold coordination. Bonds within the pyramidal ions are considered essentially covalent with some ionic character present. Their stretching is due to the intermolecular interactions but also to packing interference and, in the case of the $Bi_2Cl_8^=$ ion, to the sharing of Cl atoms.

Reliability of Model

The consistency of Bi-Bi vectors with the observed Patterson peaks, the agreement between observed and calculated

structure factors, the satisfactory progress of refinement, and the plausibility of the resulting configurations and interatomic distances all serve to insure that the proposed model is essentially correct. The residual

$$R_1 = \frac{\Sigma \left| |F_o| - |F_c| \right|}{\Sigma |F_o|},$$

expressing the degree of agreement between observed and calculated structure factors, is most commonly quoted as a measure of accuracy of a model because it is more amenable to numerical treatment than the other criteria. This residual gives a good indication of the progress of refinement but does not in itself constitute an adequate measure of the correctness of a model since all reflections, weak or strong, are assigned equal weight.

According to Lipson and Cochran (1957, p. 147), the only valid basis for the assessment of the correctness (as distinct from accuracy) of a structure lies in the agreement for individual reflections. For reflections which are reasonably strong, and thus reliably estimated, the observed and calculated structure factors should agree to within 40%, most of them being much better than this. A survey of the 55 strongest reflections showed that their structure factors, on the average, agreed within 11% and only two showed a discrepancy higher than 20%.

Several factors must be borne in mind when considering

the 15.6% value of the unweighted residual R_1 calculated by the least squares program. On the negative side of the ledger, this figure takes no account of unobserved reflections. In general, weak reflections showed poorer agreement, as indicated by the slightly higher value (18.7%) of the weighted residual R_3, so that the inclusion of unobserved reflections should be expected to increase R_1 somewhat. The implication of this fact, borne out by an inspection of positional standard deviations in Table 8, is that the stronger diffracting Bi atoms have been located more reliably than the Cl atoms.

The extenuating circumstances, on the other hand, are more numerous and more consequential. The residual was computed by forcing isotropic temperature factors on the refinement process although Figure 10 indicates considerable thermal anisotropy for Bi atoms. The absorption correction factors differed by as much as 5,000% between reflections, and a slight error in the correction curve would carry very serious consequences. Finally, no allowance was made for secondary extinction simply because no handy correction scheme is yet available. This effect is brought on by the reduction of the intensity of the primary beam incident upon a plane due to reflection from the preceding planes and is expected to be quite important for a crystal containing strongly diffracting bismuth.

Although some doubt remains as to the exact location of

the Cl atoms, special precautions, described in the refinement section, were taken to verify their number. In addition, the density of 6.56 g/cc calculated for 48 Bi and 56 Cl atoms compares much better with the 6.54 g/cc experimental value than the 6.41 g/cc figure calculated on the basis of 48 Bi and 48 Cl atoms per unit cell.

Conclusions

The establishment of atomic configuration in solid BiCl provides a foundation upon which a framework of speculation can be constructed concerning the nature of species formed when bismuth metal or BiCl is dissolved in liquid $BiCl_3$. As the vigor of disruptive forces induced by thermal motion increases with rising temperature, a process of structural breakdown and interaction of the fragments with the $BiCl_3$ solvent can be envisioned. At the melting point the intermolecular interactions are destroyed and the crystal structure collapses. There is partial disproportionation of Bi_9^{+5} to Bi metal and Bi^{+3} ions and partial dissociation of $BiCl_5^{=}$ and $Bi_2Cl_8^{=}$. The metal-rich liquid phase contains Bi_9^{+5} and Cl^- ions dissolved in the metal, the salt-rich phase is composed of Bi_9^{+5} cations and Cl^-, $BiCl_4^-$, and $BiCl_5^{=}$ anions in equilibrium with $BiCl_3$. At higher temperatures, nearly complete breakdown of all molecular species takes place to produce a single liquid phase composed of $Bi^{+\delta}$ and Cl^- ions along with

solvated metallic electrons.

The presence of all these species in Bi-$BiCl_3$ solutions, with the exception of Bi_9^{+5}, had been conjectured by researchers at one time or another. Topol et al. (1960) proposed the formation of $BiCl_4^-$ and $BiCl_5^=$ ions to account for the high cryoscopic number of alkali chlorides dissolved in molten $BiCl_3$ after detecting K_3BiCl_6 and K_2BiCl_5 in the KCl-$BiCl_3$ phase diagram. Subsequent spectroscopic work by Boston and Smith (1960) and concentration cell e.m.f. measurements of Topol et al. (1961) indicated the presence of simple species such as BiCl and $(BiCl)_3$ in very dilute solutions or at elevated temperatures and the formation of unidentified polymers at increased concentrations. The presence of Bi_9^{+5} polymers accounts for the high viscosity of the salt-rich phase while the complexity of the BiCl structure explains the marked tendency of concentrated solutions toward supercooling.

From the vantage point of an archeologist who dug for an earthen vase but ends up surveying an ancient hamlet which he has freed from its burden of overlying sand and debris, it becomes apparent that the finished product has outgrown the original scope of the investigation. What was to be a physical tool for prying into chemical secrets became an achievement which stands on its own merits, opens up a Pandora's box of exciting fact and speculation, and echoes the words of Clarence R. Wylie:

". . . Bridges stand, and men no longer crawl
In two dimensions. And such triumphs stem
In no small measure from the power this game,
Played with thrice-attenuated shades
Of things, has over their originals.
How frail the wand, but how profound the spell!"

SUMMARY

Bismuth monochloride separates out as a solid phase when bismuth metal is dissolved in liquid $BiCl_3$. Its crystals take the form of black diamagnetic needles with a flattened hexagonal cross section. The crystal structure of bismuth monochloride was determined as an aid in the identification of the species formed in the Bi-$BiCl_3$ system.

The stoichiometric formula of bismuth monochloride was found to be $BiCl_{1.17}$. The crystals are orthorhombic with lattice constants a_o = 23.057, b_o = 15.040 Å, c_o = 8.761 Å and space group Pnnm. The experimental density of 6.54 g/cc agrees well with the 6.56 g/cc value calculated on the basis of the 48 Bi and 56 Cl atoms per unit cell. Three-dimensional Weissenberg and precession film data were obtained with Cu Kα radiation. The 2500 reflections were judged visually, and corrected for the Lorentz factor, polarization, absorption, and multiplicity.

The structure was determined by the heavy atom technique. Interpretation of a three-dimensional Patterson map located all 48 Bi positions and thus established the phases of the more important reflections. The 56 Cl positions were found through three-dimensional Fourier and difference Fourier maps. Refinement of the structure was carried out by the least squares technique using isotropic temperature factors. All positions refined satisfactorily resulting in a final R_1

value of 0.156.

Each unit cell contains four Bi_9^{+5} cations in the shape of distorted trigonal prisms that have a Bi atom projecting from each face. There are also eight $BiCl_5^{=}$ and two $Bi_2Cl_8^{=}$ anions where the Cl atoms assume a distorted tetragonal pyramidal configuration about Bi. The cation has delocalized bonding and a charge of +5 based on the assignment of Bi(III) atoms to the anions. The latter are thought to have conventional Bi-Cl bonds. Intermolecular linkage is provided by weak Bi-Cl interactions which are considerably shorter between anions than between an anion and the cation. They are responsible for the configurational distortions. A mode of structural breakdown with rising temperature is proposed and the species formed by interaction of the fragments with the $BiCl_3$ solvent are compared with results of previous investigations.

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Finally, I wish to express my sincere gratitude to my many friends and associates at the Ames Laboratory for their stimulating discussions, gracious assistance, and gratifying companionship.

APPENDIX A: COMPUTER PROGRAMS

Absorption Correction and Sharpening Program

Introduction

This program applies spherical or cylindrical absorption corrections to observed Weissenberg intensities and structure factors and/or multiplies intensities by an optional sharpening factor. A provision is included for multiplying intensities and structure factors by a constant during either operation.

Description of input cards

Absorption correction deck (15 cards)

/ $A^*(10)$,PP/ in fields 1-7.

A^* is the absorption correction at .01 increments of $\sin^2\theta$, as described in the discussion section. PP = 50 + p, where p is the power of 10 multiplying $A^*(10)$. These cards must be left out if absorption correction is not desired.

Constant cards

/ $\cos^2\nu$ (10),PP/ $\cos\nu$ (10), PP / K_a (10), PP/

ν is defined in the discussion section, K_a is a constant which multiplies the absorption-corrected intensities. This card must be left out if absorption correc-

tion is not desired.

/$\pm$B'/λ^2(10), PP/$\sum_i Z_i \cdot 10^6$(10), PP/n_1(10), PP/n_2(10), PP/

/n_3(10), PP/n_4(10), PP/K_s(10), PP/

$\pm$B'/λ^2 is the artificial temperature factor defined in the discussion section, $\sum_i Z_i$ is the sum of atomic numbers for all atoms in the unit cell, n_i is the number of atoms of the i-th type in the unit cell (in the same order as the scattering factors), K_s is a constant which multiplies the sharpened intensities and sets K_a = 1 if both are included. This card must be left out if sharpening is not desired.

Data cards

/hhkk$\ell\ell$aaaa/I_o(7)/$\sin^2\theta$(10)/f_1(6)/f_2(6)/f_3(6)/f_4(6)/

aaaa = anything, I_o is the unprocessed intensity, f_i is the scattering factor for the atom of type i. These cards have the same format as the INCOR-IM output cards.

Operating instructions

Loading sequence

1. ACS Program deck
2. Switch card
3. Absorption Correction deck (optional)
4. Control cards #1 and/or #2
5. Data cards

Console settings

Storage entry: 70 1952 9999 (00 0000 1999 if program loaded)

Programmed:	STOP	Display:	PROGRAM
Half cycle:	RUN	Overflow:	SENSE
Control:	RUN	Error:	STOP

Operation

Use FORTRANSIT OBJECT wiring panel.

A machine stop with 0050 or 0051 in address lights indicates error in the format of absorption correction or constant cards.

Computation times are 2.1 sec. per reflection for absorption correction and 2.3 sec. per reflection for the sharpening operation.

Description of output cards

/hhkk$\ell\ell$aaaa/I_c(7), F_o(2)/$\sin^2\theta$(10)/f_1 (6)/ etc.

I_c is the absorption corrected and/or sharpened intensity. These output cards are in the proper format for input to the LS-IIM2 least squares program.

Discussion

Absorption corrections are calculated according to the method developed by Bond (1959). The correction factor A^*, defined as the ratio of the corrected to the observed

intensity, is listed in Bond's paper as a function of μR and $\sin^2\theta$. μ is the linear absorption coefficient and R is defined by the relation

$$R = R_o \sec \nu$$

where R_o is the radius of the crystal cylinder and ν is the angle between the incident x-ray beam and a plane normal to the cylinder axis. For spherical crystals and for zero layer photographs of cylindrical crystals $\nu = 0$, $\sec \nu = 1$, and $R = R_o$.

For higher layer reflections, the absorption correction factor undergoes the transition

$$A^*(\mu R_o, \theta) \longrightarrow \cos \nu \cdot A^*(\mu R, \tau/2).$$

τ is related to ν and θ by the expression

$$\cos \frac{\tau}{2} = \frac{\cos \theta}{\cos \nu} \quad \text{or} \quad \sin^2 \frac{\tau}{2} = 1 - \frac{1 - \sin^2 \theta}{\cos^2 \nu}$$

The program calculates $\sin^2(\tau/2)$ and selects the corresponding value of A^* by linear interpolation. In the case of spherical crystals, again $\nu = 0$ so that $\sin^2(\tau/2) = \sin^2\theta$.

Absorption correction decks are prepared by reading values of A^* from plots of A^* vs. $\sin^2\theta$, at .01 increments of $\sin^2\theta$, between 0.00 and 1.00. A new plot is required for each value of μR. Some judgement must be exercized in choosing the scale of the absorption correction factors in order to obtain the desired number of significant figures in the output.

"Sharpening" of intensities is performed according to the

relation:

$$F_o^2\,(\text{sharp}) = \frac{F_o^2}{(\Sigma_i f_i/\Sigma_i Z_i)^2} \exp \pm B^1 \frac{(\sin\theta)^2}{\lambda^2}$$

where f_i is the scattering factor and Z_i, the atomic number of the i-th atom and $\pm B^1$ is the artificial temperature factor.

Since the scattering factors decrease as θ increases, both the ratio of sums and the exponential term in the above expression tend to increase the value of intensity at higher angles whenever the artificial temperature factor is positive. The negative temperature factor is often used to diminish the sharpening effect of the ratio of sums. If no other guide is available B^1 may be tentatively adjusted so that the condition

$$\sum_{S_o-.1}^{S_o} \langle F^2\,(\text{sharp}) \rangle = .1 \sum_i Z_i^2$$

holds, where $S_o = \frac{\sin\theta\max}{2}$.

Program listing (in FORTRANSIT language)

```
0 0 DIMENSION ABCO (101)
0 0 READ, SWC1, SWC2
0 0 IF (SWC1) 1, 2, 1
1 0 READ, ABCO
0 0 READ, CSNU, CNU, CONST
0 0 IF (SWC2) 2, 3, 2
```

```
2 0  READ, BOLSQ, SAN, ATK1,
0 1  ATK2, ATK3, ATK4, CONST
3 0  READ, IND, INSFP, ISST
0 1  H, ISCF1, ISCF2, ISCF3,
0 2  ISCF4
0 0  VINT = INSFP*1.E-7
0 0  CINT = VINT
0 0  SSTH = ISSTH*1.E-10
0 0  IF (SWC1) 4, 5, 4
4 0  ASSUP = 1.-((1.-SSTH)/
0 1  CSNU)
0 0  JSSUT = ASSUP*1.E2
0 0  VINT = (ABCO(JSSUT + 1)
0 1  -(ASSUP*1.E2 - JSSUT)*
0 2  (ABCO(JSSUT + 1) - ABCO(
0 3  JSSUT + 2)))*CNU * VINT
0 0  CINT = VINT
5 0  IF (SWC2) 7, 8, 7
7 0  SHFC = SAN/(ATK1*ISC
0 1  F1 + ATK2 * ISCF2 + ATK3
0 2  * ISCF3 + ATK4 * ISCF4)
0 0  CINT = SHFC * SHFC * EXPF
0 1  (BOLSQ * SSTH) * VINT
8 0  VINT = CONST * VINT
0 0  STFC = SQRTF(VINT)
```

```
    0  0 CINT = CONST * CINT
    0  0 INTM = CINT * 1.E2
    0  0 INTP = INTM * 100000
    0  0 ISFP = STFC * 1.E2
    0  0 INSFP = INTP + ISFP
   10  0 PUNCH, IND, INSFP, ISS
    0  1 TH, ISCF1, ISCF2, ISCF
    0  2 3, ISCF4
    0  0 GO TO 3
    0  0 END
```

Standard Deviations Program

Introduction

The STD program computes standard deviations of observed structure factors on the basis of uncorrected film data. The output is easily reproduced into the standard input format of the I.B.M. 704 Crystallographic Least Squares Program (Busing and Levy, 1959).

Description of input cards

Constant card

/ I_b (7) /

I_b is value of the median intensity of the best judged range. It often coincides with 16 times the lowest ob-

servable intensity.

Data cards

/ hhkk$\ell\ell$aaaa / I_o (7) /

I_o is the uncorrected value of the observed intensity, aaaa = anything. These cards have the same format as the INCOR-I (Zalkin and Jones, 1957) data input cards.

/ hhkk$\ell\ell$aaaa / I_c (7), F_o(2) / a'a' $\cdots$ a' $\begin{matrix}8\\9\end{matrix}$ /

I_c is the corrected value of the observed intensity, F_o is the observed structure factor ($= \sqrt{I_c}$), 8 in col. 30 indicates $I_o \geq I_b$, 9 indicates $I_o < I_b$. Both the INCOR-I and the ACS output cards have the proper input format. These two types of data cards must appear in pairs with matched indices and in the order given.

Operating instructions

Loading sequence

1. STD Program deck, 2. Control card, 3. Data cards

Console settings

Storage entry: 70 1952 9999 (00 0000 1999 if program deck is already loaded).

Programmed:	STOP	Display:	PROGRAM
Half cycle:	RUN	Overflow:	SENSE
Control:	RUN	Error:	STOP

Operation

Use FORTRANSIT OBJECT wiring panel.

A legitimate machine stop is probably due to mismatched indices in data cards.

Computation times are 1.0 sec. per reflection for $I_o \geq I_b$, 2.5 sec. per reflection for $I_o < I_b$.

Description of output cards

/ hhkkℓℓaaaa / F_o (2)/ $\sigma(F_o)$(3)/

$\sigma(F_o)$ is the standard deviation of the observed structure factor.

Discussion

This program was designed primarily for use in conjunction with the Crystallographic Least Squares Program by Busing and Levy which employs the $\sigma(F_o)$ values for regulating the contribution of each reflection in the expression

$$R = \Sigma \left[\frac{1}{\sigma(F_o)} (|F_o| - |F_c|)\right]^2.$$

R is the function minimized with respect to crystallographic parameters by the least squares refinement, F_o and F_c are the observed and calculated structure factors, respectively.

The standard deviation of the best judged intensities ($I_o \geq I_b$) was estimated at 10%, that of the poorest judged (lowest observable), at 80%. Accordingly, this function was

expressed by

$$\frac{\sigma(I_o)}{I_o} = \begin{cases} 0.1 & \text{for } I_o \geq I_b \\ 0.1 \left(\frac{I_b}{I_o}\right)^{3/4} & \text{for } I_o < I_b \end{cases}$$

It was learned that the experimental errors of the corrections applied to I_o to obtain $I_c (= F_o^2)$ are much smaller than the error inherent in the visual judgement of intensities and can therefore be neglected. On the basis of this information and a standard statistical relation, one can write

$$\frac{\sigma(F_o)}{F_o} \cong \frac{\sigma(F_o^2)}{\frac{1}{2} F_o^2} = \frac{1}{2} \frac{\sigma(I_c)}{I_c} \cong \frac{1}{2} \frac{\sigma(I_o)}{I_o}$$

or

$$\sigma(F_o) = \begin{cases} .05\ F_o & \text{for } I_o \geq I_b \\ .05 \left(\frac{I_b}{I_o}\right)^{3/4} \cdot F_o & \text{for } I_o < I_b \end{cases}$$

The calculation of $\sigma(F_o)$ is performed according to these relations.

Program listing

Following is a FORTRANSIT listing of all program steps, along with comments explaining each operation.

```
0 0  READ, INB                    read Ib
1 0  READ, IND, INT               read uncorrected data
0 0  READ, JND, JNSF, JSSTH       read corrected data
```

```
0 0   IF (IND-JND) 2, 3, 2          test for properly matched
                                    indices
2 0   STOP
3 0   LSF = JNSF * 1000000          isolate F_o ...
0 0   NSF = LSF / 1000000           then shift back
0 0   LOD = JSSTH * 1000000000      isolate breaking code ...
0 0   KOD = LOD / 1000000000        then shift back
0 0   IF (KOD-8) 4, 4, 5            branch on breaking code
4 0   NSD = NSF / 2                 calculate std. dev. for
                                    I_o ≥ I_b
0 0   GO TO 6
5 0   L = INT / 1000                 float 1000 I_b/I_o
0 0   A = INB / L
0 0   NSD ((A**.75)*NSF)            calculate std. dev. for
                                    I_o < I_b
0 1   / 353                         353  1000 x 2
6 0   PUNCH, IND, NSF, NSD          punch indices, F_o, σ(F_o)
0 0   GO TO 1
0 0   END
```

APPENDIX B: OBSERVED AND CALCULATED STRUCTURE FACTORS

HKO STRUCTURE FACTORS FOR BISMUTH MONOCHLORIDE

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
2	748	645-	318	278	239-	617	174	135	912	241	264-
4	558	636-	4	728	610-	618	95	93-	914	430	402
6	239	292	4 1	143	97	7 1	281	241-	915	84	115
8	381	449-	4 2	402	370-	7 2	183	157-	916	106	23
10	229	304-	4 3	612	565	7 3	865	924	917	112	104-
12	180	250	4 4	453	385	7 4	690	678	10	455	403-
14	107	108	4 511091113-			7 5	986	864-	10 1	163	143-
16	326	378-	4 6	171	136	7 6	513	424-	10 2	9081047	
18	253	258	4 7	562	518	7 7	254	182-	10 3	103	65-
1 3	336	422	4 8	300	286	7 9	603	572	10 4	331	286-
1 4	93	64	4 9	519	472	710	265	269-	10 5	197	140-
1 5	513	610	411	438	516-	711	409	402	10 6	175	158-
1 6	90	75-	412	126	115	712	104	126	10 7	166	140-
1 7	308	379-	413	188	242	713	222	260-	10 8	157	105
1 8	274	405	416	122	94-	714	218	148-	10 9	190	117-
1 9	124	62-	417	211	193-	715	90	52-	1010	333	260-
110	112	155-	418	95	110	716	131	136	1011	155	71
111	495	681-	419	136	128-	717	129	118	1016	79	100
112	96	75	5 1	108	88	718	144	91	1017	102	119
113	231	248	5 2	142	124-	8	678	744-	11 1	482	526
116	253	245-	5 3	748	749-	8 1	118	99-	11 2	8591004-	
117	142	136	5 5	181	130-	8 3	147	97	11 3	102	77-
2 2	280	272	5 6	103	68	8 4	171	142	11 4	313	272
2 4	467	536	5 7	427	365	8 5	205	146-	11 6	428	308
2 5	620	736	5 9	337	330	8 6	489	378	11 7	265	228
2 6	8901206-		510	222	253-	8 7	175	92	11 8	734	656-
2 7	154	117	511	188	173	8 8	270	281-	11 9	902	880-
2 8	176	224	512	468	487	8 9	405	320-	1110	243	297
2 9	272	283-	513	176	146	811	95	79-	1111	152	138
210	407	477	514	240	275-	814	151	106-	1112	259	251
211	494	603	515	171	154-	815	71	49-	1113	91	88-
212	220	278-	517	197	140-	816	350	294	1114	231	268-
215	360	391-	518	47	78	817	259	275	1115	149	143
217	110	96	519	82	100	818	82	89-	1116	164	83
219	144	174-	6	514	404-	9 1	509	544	1117	40	3
3 2	133	122-	6 1	823	864-	9 2	664	663	12	204	217
3 3	567	557-	6 2	528	547-	9 3	163	144-	12 1	124	114
3 4	261	260	6 3	525	489	9 4	321	280-	12 2	558	617
3 5	799	872	6 4	240	208	9 5	409	351-	12 3	101	17
3 6	348	391-	6 5	243	126	9 6	685	613-	12 4	268	290-
3 7	162	192-	6 6	872	837	9 7	307	270	12 5	189	84-
3 8	601	759	6 8	151	136	9 8	654	584	12 6	86	54-
3 9	281	269	610	252	213-	9 9	335	286-	12 8	277	173-
310	86	65	611	108	108-	910	432	395-	12 9	293	216
316	77	52-	614	241	250	911	171	167	1210	133	47

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
1211	101	18-	1515	163	148-	19 7	161	119-	2310	65	48
1212	74	61	1516	87	75-	19 8	221	225-	2311	104	82-
1213	141	170	16	459	450-	19 9	86	120	2312	91	56-
1214	299	254-	16 1	238	245	1911	72	93	24 1	250	266
1216	60	70	16 2	85	57-	1913	74	17	24 3	225	207
1217	252	248-	16 3	261	268-	1914	80	47	24 4	145	118
13 1	507	583-	16 5	426	391	20	646	737	24 5	361	334-
13 2	263	238	16 6	166	117	20 2	259	263-	24 6	189	133-
13 3	1110	1180	16 7	105	37	20 3	170	199-	24 7	291	228
13 4	486	475-	16 8	189	187	20 4	89	75-	24 8	104	109
13 5	218	177-	16 9	270	270-	20 6	241	244	24 9	148	84
13 6	511	408	1610	239	199	20 8	177	147-	2410	60	35-
13 8	286	284	1611	166	198	2010	244	240-	2411	86	90-
1312	124	81-	1612	113	110	2011	236	137-	25 2	183	188-
1313	319	289-	1614	80	32-	2012	90	110	25 3	111	83-
1315	240	232	1615	144	129-	2014	156	178	25 4	219	161
1316	92	105-	17 1	155	106-	21 1	77	114	25 5	161	183
1317	59	47	17 3	161	130-	21 3	174	193	25 6	150	85
14	189	224	17 4	127	140	21 4	129	108-	25 7	90	15
14 1	290	323	17 5	107	59	21 6	98	84-	25 8	110	113
14 3	100	71-	17 6	149	188	21 7	303	208-	25 9	110	80
14 4	440	435-	17 7	79	37-	21 8	119	82-	2510	56	9-
14 5	311	307	17 8	494	458-	21 9	175	178	26	112	99
14 6	395	354	17 9	254	261	2111	247	253-	26 1	251	239-
14 7	137	146-	1710	228	138	2112	144	107	26 2	200	168-
14 9	209	164	1711	139	122	2113	129	108	26 3	242	272
1410	90	91	1713	130	98-	22	153	125	26 4	54	82-
1411	287	196	1715	95	72	22 1	265	292-	26 5	222	192
1412	97	90	18	273	369-	22 3	185	166-	26 6	170	144
1413	266	171-	18 1	290	310	22 4	410	354	26 7	139	135-
1414	70	124-	18 3	95	120-	22 5	161	132	26 8	125	136
1416	88	32-	18 4	233	265	22 6	327	272-	26 9	60	14
1417	164	181-	18 5	81	127-	22 7	177	135-	27 1	168	162-
15 1	150	142-	18 6	247	244-	22 8	109	112-	27 2	94	31
15 2	200	190	18 8	114	111	22 9	90	114-	27 6	62	61
15 3	507	442-	18 9	153	144	2210	194	168	28	135	106-
15 5	177	148	1811	386	277-	2211	290	258	28 1	84	57-
15 6	175	104	1812	82	29-	2212	148	158-	28 2	41	49-
15 7	721	674	1813	102	129-	23 1	164	136	28 3	107	128
15 8	156	124	1814	187	132	23 2	88	105-	28 4	40	46
15 9	242	250-	1815	279	260	23 3	109	69-	28 5	39	54-
1510	259	225	19 1	157	201	23 5	261	242			
1512	327	304-	19 2	354	350	23 6	157	132-			
1513	280	234	19 3	140	128-	23 7	120	105-			
1514	160	147	19 4	196	162-	23 8	236	202			

HK1 STRUCTURE FACTORS FOR BISMUTH MONOCHLORIDE

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
9	189	213	317	164	144	611	132	143-	911	163	131
11	112	105-	318	123	91	612	240	259	912	256	187
13	446	551	319	25	37	613	102	63-	914	151	97
15	94	71	402	398	412	614	145	179-	917	60	20
17	89	92-	404	208	194-	615	231	232-	1001	277	310
1 2	343	430-	405	275	290	617	52	37	1002	214	238-
1 3	443	536-	406	680	692-	618	54	53	1003	452	462-
1 6	96	36-	407	123	83-	700	290	296-	1006	206	176
1 8	158	197-	408	73	6-	702	135	134	1007	125	17
1 9	121	100-	409	166	159	703	675	711	1008	460	418
110	122	149	410	84	81-	704	324	271	1009	188	193-
111	195	272	411	165	179-	705	160	137	1010	97	99-
112	129	131	412	306	323	707	244	221	1011	361	405
113	96	138-	413	216	276-	708	176	157-	1012	222	184-
114	116	146	414	75	67	709	264	212-	1013	97	66
115	100	55-	415	92	109	710	185	207	1014	99	68-
117	179	211	417	117	102-	711	225	204-	1015	107	70
119	69	104-	418	129	123-	712	246	254-	1017	51	15
2 2	227	237-	500	341	326	713	121	132	1100	576	690-
2 3	210	227-	501	728	854-	714	124	128-	1102	211	200
2 5	126	151	502	148	32-	715	144	153-	1103	168	171
2 6	680	831-	503	125	35	716	156	150	1104	137	172-
2 7	184	218-	504	162	170-	717	44	15-	1105	89	29
2 8	269	306-	505	143	130	718	150	144-	1106	244	182-
2 9	93	104-	506	287	263	801	177	156-	1107	253	198-
210	205	184	507	130	118-	802	288	294-	1108	106	135
211	134	157	508	131	77	803	563	564	1109	110	32-
212	287	320	509	233	213	804	643	609	1110	102	148-
214	206	211	510	295	250-	805	493	483-	1111	195	179
215	102	34-	511	118	120-	806	244	212	1112	234	182
217	108	93	512	162	128-	807	155	159-	1113	200	140
218	39	32-	513	156	128-	808	491	444	1114	216	229
219	81	55-	514	157	190-	809	191	140	1115	116	119-
3 3	670	721-	515	114	104	811	153	95-	1117	129	93-
3 4	172	132	516	130	167-	812	377	341-	1201	196	156-
3 5	831	984-	517	118	84	813	125	93-	1202	241	298-
3 6	219	247-	518	83	59	814	166	129-	1204	245	257-
3 7	466	516	601	125	148	818	34	16-	1205	207	193-
3 8	277	294	602	125	102	901	422	469	1207	110	99-
3 9	138	110	604	84	55	903	692	715	1208	173	156-
311	203	220-	605	163	126	905	171	141	1209	204	183
312	108	59-	606	207	154	906	164	153	1210	160	149
313	136	155	607	387	367	908	323	223-	1211	178	150
315	101	38	609	241	226-	909	257	195-	1212	224	179
316	84	88-	610	300	290-	910	227	174-	1214	113	130-

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
1215	146	132	16 3	196	160	20 5	153	159-	2411	64	85
1216	139	127	16 4	439	451	20 6	197	231	25 1	96	105-
13 1	322	335-	16 5	219	258	20 7	62	73-	25 2	84	60-
13 2	136	138-	16 6	122	158-	20 8	67	31-	25 5	74	68-
13 3	374	364-	16 8	436	421-	2010	121	100	25 6	134	131
13 4	120	78-	16 9	145	84-	2011	83	51-	25 7	120	91-
13 5	310	262-	1610	110	138	2013	158	177	25 8	128	96
13 6	200	145	1611	217	207-	2014	122	138-	2510	81	96-
13 7	338	323-	1614	134	110	21	172	207	26 3	80	5-
13 9	312	231	17	150	176	21 2	266	321-	26 4	152	140-
1310	277	213	17 1	82	49	21 3	73	102	26 5	99	104
1311	74	58	17 2	105	79	21 5	135	121	26 8	66	77-
1312	75	74	17 3	152	190-	21 6	101	130	27 1	142	154-
1314	85	104-	17 5	225	281	21 7	63	70-	27 2	61	73
1315	180	139	17 6	71	78-	21 8	252	207-	27 3	73	53
1316	85	92	17 7	77	113	2110	80	33	27 4	56	35
1317	62	28-	17 8	71	33	2111	74	97	27 6	85	99-
14 1	201	207-	17 9	86	89-	2112	134	61	27 7	95	81-
14 2	244	274	1710	116	71-	2113	44	18	28 3	155	161
14 3	84	49-	1712	85	4	22 2	108	152-	28 4	145	149
14 4	396	438-	1713	231	167-	22 4	121	107-	29	219	280
14 6	230	218-	1714	183	160-	22 5	184	216-	29 1	103	103
14 7	353	349	18 2	451	534	22 7	66	91-	29 3	74	62
14 8	175	155-	18 5	287	269	22 8	152	143			
14 9	197	148-	18 6	266	236	22 9	271	220			
1410	72	24-	18 7	242	234-	2210	121	56			
1412	105	100	18 8	81	66	2211	73	59			
1413	139	104	18 9	134	81-	2212	51	29-			
1414	229	208	1810	163	128-	23	246	339-			
1415	131	149-	1812	94	77-	23 1	98	145			
1416	34	24-	1813	161	106-	23 3	113	101-			
1417	42	24	1814	77	56	23 4	90	147			
15	212	270	1815	43	30	23 5	119	161-			
15 1	127	120	19 1	125	147	23 6	106	70-			
15 3	471	511-	19 2	168	158	23 8	132	110			
15 4	153	127-	19 3	191	210	23 9	147	84-			
15 5	168	176-	19 4	115	121	2310	54	41			
15 6	105	53	19 5	153	140	2311	90	111			
15 7	276	242	19 6	203	216-	24 2	206	222-			
15 8	122	95	19 9	143	155	24 3	212	208-			
1510	93	45	1910	85	65-	24 4	71	52-			
1512	210	153-	1911	171	177-	24 6	201	174-			
1514	178	105-	1912	77	61-	24 9	124	126			
16 1	124	94-	1913	52	46-	2410	119	89			
16 2	131	100-	1914	118	94						

HK2 STRUCTURE FACTORS FOR BISMUTH MONOCHLORIDE

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
2	774	739	4 2	302	336-	616	175	188	917	52	43
6	483	553-	4 3	447	511-	617	66	73-	918	155	179
8	337	448-	4 4	220	165-	618	207	199-	10	540	532
10	404	504	4 5	685	682	7 1	336	359	10 2	251	251
12	135	126-	4 6	523	514	7 2	208	183	10 3	155	150-
14	286	403-	4 7	138	132-	7 3	733	755-	10 4	77	107
16	238	278	4 8	118	75	7 5	296	256-	10 5	211	188
18	39	65-	410	276	282-	7 7	458	410	10 6	564	470-
1 2	78	17-	411	303	297	7 8	570	599-	10 7	261	175-
1 3	288	246	412	205	236	710	197	155	10 9	213	148-
1 4	216	224-	413	180	123-	712	179	182-	1010	239	207-
1 5	79	41-	415	111	130-	713	333	337	1011	190	140
1 7	155	199	416	129	145-	714	84	96	1012	175	115-
1 9	483	650-	417	130	145-	715	327	327-	1013	108	101-
111	213	216-	418	87	100	716	116	130	1014	150	110
114	171	153	5 1	509	529-	717	87	63-	1016	69	104-
115	109	70	5 2	9601	134	718	68	58	1017	78	64
116	157	143-	5 3	152	126-	8	453	413	11 1	98	120
118	38	55-	5 4	671	687-	8 1	537	557	11 2	169	135
2 1	646	807	5 5	273	258-	8 2	531	565-	11 4	421	392-
2 2	414	366	5 6	378	331	8 3	345	342-	11 5	436	401
2 4	565	611-	5 7	109	104-	8 4	78	94	11 6	159	113-
2 5	397	483-	5 8	145	139	8 5	371	306-	11 7	565	495-
2 6	78	81-	5 9	614	577	8 6	341	253	11 8	414	366
2 7	435	508	510	141	137-	8 7	145	104	11 9	215	161-
2 9	221	254	511	314	286	8 8	338	258-	1110	109	15-
210	184	224-	513	215	188-	8 9	211	176-	1111	196	161-
215	80	46	514	117	182	810	196	144-	1112	210	155-
216	104	100-	515	104	69-	811	206	184-	1113	111	104-
217	149	194-	516	119	115-	813	80	19	1114	143	76
3 2	392	422-	517	68	47-	814	127	96	1115	98	86
3 3	144	129	6	11901	555-	815	132	121	1116	86	52
3 4	442	421	6 1	80	153	817	104	100	1117	82	74
3 5	79	49	6 2	259	261-	9 2	351	345-	12	545	658
3 6	325	312	6 3	299	257-	9 3	395	378	12 1	233	209-
3 8	287	282-	6 4	642	636	9 4	334	283	12 3	211	180
3 9	152	120-	6 5	336	256	9 6	76	84	12 4	128	149-
310	411	481	6 7	128	169-	9 7	647	564-	12 6	320	204-
311	191	159	6 8	216	176	9 8	604	516-	12 7	188	163-
313	187	238-	6 9	208	230	9 9	348	294	12 9	202	102
315	87	93	610	314	314	910	121	80	1213	155	143
316	124	108-	611	144	92-	911	177	151-	1214	77	73-
318	127	89-	612	216	214-	913	142	124-	1215	70	33-
4	347	312-	613	195	209-	914	106	81	1216	189	130-
4 1	210	198-	614	108	90	915	120	120	1217	177	133-

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
13 2	222	211-	1609	82	44-	2005	269	265-	2603	96	137
13 3	251	205-	1611	291	200-	2006	183	167-	2605	128	110
13 4	230	272-	1612	166	137	2008	207	218-	2606	69	66-
13 5	331	306	1613	56	69	2010	72	69	2607	104	127-
13 6	299	237	1615	50	58-	2011	271	217-	2608	41	84
13 7	267	197	1701	131	162-	2012	167	104-	2702	78	72
13 8	306	255	1702	269	298	2013	107	89	2703	186	188-
13 9	244	215-	1703	129	104-	2103	315	312	2704	38	36-
1311	455	356-	1704	72	121	2105	338	330-	2706	164	181
1312	164	161	1705	127	103-	2106	103	116-	2707	141	154
1313	261	274	1706	289	262-	2108	125	74-	2800	100	99
1314	160	171-	1708	339	280	2109	132	111-	2801	133	144
1315	70	59-	1709	219	227	2111	106	95-	2802	141	148-
1316	69	69-	1710	226	234-	2112	112	93	2901	77	90-
14 1	186	186-	1711	153	128	2200	296	270			
14 2	135	119-	1713	99	111-	2201	110	76			
14 3	309	298	1715	72	87	2202	77	80			
14 4	165	149	1800	379	401-	2203	131	104-			
14 6	302	261-	1801	460	535-	2204	142	120-			
14 8	100	12-	1804	178	151-	2205	177	160-			
14 9	115	38	1805	287	248	2206	131	134			
1410	364	324	1806	141	119	2207	89	75			
1411	157	113	1807	160	170-	2208	188	167-			
1412	165	213-	1808	168	123	2210	143	119-			
1414	162	122-	1809	182	115-	2211	92	36			
1415	175	86-	1810	260	180-	2302	128	163-			
15 1	338	377-	1812	77	106	2304	90	101			
15 2	431	448-	1813	69	94-	2309	154	154-			
15 3	125	104	1814	89	98	2311	30	17			
15 4	458	440	1901	204	230	2312	9	25-			
15 6	72	34-	1902	117	131	2400	120	132-			
15 7	119	54	1903	227	259-	2402	130	125			
15 8	124	78	1905	112	116-	2403	63	41-			
15 9	120	64	1906	159	120-	2404	81	97-			
1510	156	125	1907	96	85	2405	128	120			
1514	165	160-	1908	159	158-	2410	51	66-			
1515	82	95-	1909	178	136-	2501	107	149-			
16 1	323	369	1910	110	175-	2502	77	60			
16 2	262	310-	1911	284	197	2504	77	101-			
16 3	310	292	1912	231	181	2505	100	96			
16 4	122	150-	1913	40	10	2506	156	111			
16 5	314	305-	1914	50	26-	2508	67	105			
16 6	347	317	2000	236	278-	2509	89	63			
16 7	473	410	2001	149	160-	2600	203	193-			
16 8	166	101	2002	205	227	2004	166	152			

HK3 STRUCTURE FACTORS FOR BISMUTH MONOCHLORIDE

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
1	398	476-	3 8	386	320	617	108	115	915	144	176-
311	841	239	310	234	216-	618	73	52-	916	37	28
5	911	919-	311	89	105	7	801	853	917	72	72
7	138	125-	312	101	164	7 1	800	835	10 1	88	100
9	189	166	316	102	50-	7 2	309	311-	10 2	187	194-
11	296	378	317	128	98	7 3	186	180	10 3	371	289-
15	304	290	4 1	106	118-	7 5	268	218	10 4	198	155-
1 1	335	285	4 3	174	151	7 6	328	279	10 5	409	310
1 2	259	213	4 5	215	160	7 7	154	198	10 6	229	242
1 3	507	533-	4 6	88	58	7 8	180	91-	10 7	449	538-
1 4	322	290-	4 7	97	41	710	114	104-	10 8	244	229
1 5	265	222-	4 8	761	982-	711	216	219-	10 9	402	357
1 6	264	234	410	335	357	713	90	52-	1010	109	20
1 7	115	116	411	79	3	714	86	86	1011	209	192
1 8	282	245-	412	287	324	716	108	97-	1012	223	205-
1 9	147	128	413	287	317-	717	218	185-	1017	168	127
110	155	138	415	90	147	718	54	38-	11	223	220-
112	168	179	417	94	84-	8 1	127	118	11 1	396	392
113	230	218-	5	308	296-	8 2	266	249-	11 2	151	112-
115	166	139	5 2	292	304	8 4	526	513	11 3	324	332
116	236	232	5 3	509	481-	8 6	522	497	11 4	330	329
117	81	52	5 4	268	283	8 9	221	184	11 5	506	545-
118	71	108-	5 5	194	162	810	105	127	11 6	539	530-
2 1	412	356	5 6	202	182-	811	340	336-	11 8	195	173
2 2	517	489	5 7	156	177-	812	339	365-	11 9	181	196
2 3	570	527-	5 9	300	309	813	115	217	1110	76	43
2 4	346	331-	510	136	128	814	84	86-	1111	200	172-
2 5	170	108-	511	125	116-	815	77	64-	1113	235	194
2 6	594	686-	512	266	265-	816	97	38-	1114	297	306
2 7	440	534	513	189	195-	817	66	61-	1115	77	63
2 9	528	626-	514	243	280-	9	179	144	1116	60	29-
210	144	176	515	196	249	9 1	223	149	1117	160	165-
211	279	338	516	78	38	9 2	133	143-	12 1	167	139
213	198	151	517	67	63-	9 3	254	232	12 2	211	190-
214	474	429	518	58	35	9 4	392	376	12 3	356	313-
216	130	105-	6 2	716	807	9 5	770	812	12 4	276	280-
217	58	45-	6 3	408	375	9 6	314	256-	12 5	84	128
218	141	123-	6 4	476	519-	9 7	372	300-	12 6	162	113-
3	595	482-	6 6	358	342	9 8	150	96-	12 8	89	75
3 2	476	460	6 7	149	121	9 9	415	413-	12 9	245	221
3 3	941	1176-	611	161	124-	910	88	84	1210	153	69
3 4	463	429-	612	207	180-	911	398	475	1211	171	126-
3 5	212	211-	613	151	176-	912	111	74	1212	147	137
3 6	320	297	614	180	136	913	85	108-	1213	257	233
3 7	169	175	615	157	152-	914	228	147	1214	109	116-

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
1215	55	22	1610	148	110-	2104	79	70-
1216	127	141	1611	168	169-	2105	88	75-
13	748	912	1614	166	150	2106	201	207
13 1	558	648-	1700	293	298	2108	224	190-
13 2	547	598-	1701	127	88-	2109	112	108
13 3	153	128-	1702	105	74	2112	145	112
13 4	94	99-	1703	194	164	2201	114	114
13 5	72	74-	1704	178	169-	2202	104	43
13 6	375	340	1705	248	173-	2203	130	90-
13 7	328	316-	1706	179	141	2204	227	222-
1311	138	141	1707	297	263	2205	226	261-
1312	144	137	1708	133	56	2206	72	47-
1314	85	108	1709	72	8	2207	245	211
1316	137	139-	1710	282	204-	2208	185	216
14 1	254	245-	1711	176	212-	2211	138	125
14 2	202	184-	1714	103	100-	2300	293	336-
14 3	103	53	1801	261	245	2302	122	76
14 5	130	131	1802	150	142	2303	189	181-
14 6	297	293-	1803	101	155-	2304	86	58-
14 8	94	67-	1804	290	273	2306	88	97
14 9	191	173	1805	133	146	2308	78	91
1410	214	164-	1806	196	147	2309	171	114-
1411	124	155-	1809	331	313-	2402	299	344-
1412	282	342	1810	194	197-	2403	72	56-
1413	136	103	1812	119	136	2407	94	73
1415	111	134-	1813	46	20-	2408	211	243-
1416	58	31-	1814	112	113-	2500	212	229-
15	156	126-	1900	177	170-	2501	62	68
15 1	271	255-	1901	220	215-	2502	93	86
15 3	160	169-	1902	277	296	2503	103	132-
15 4	286	261	1903	284	285	2505	41	20-
15 5	261	240-	1904	96	57	2601	65	80-
15 6	262	258-	1905	209	242	2602	167	207
15 7	234	235	1906	107	109-	2603	142	102
15 8	207	122	2003	327	366	2604	283	262-
1510	309	305	2004	168	117	2605	64	64
1512	271	255-	2005	329	325-	2606	60	51
1514	174	146-	2006	78	100	2700	118	134
1515	73	62-	2008	123	98	2701	53	35
16 3	140	120	2009	82	81	2703	49	51-
16 4	294	277	2011	88	143	2704	77	78-
16 5	289	277	2013	55	49-	2705	87	73
16 6	410	507-	2100	113	121-	2801	45	28
16 8	156	124	2101	83	141	2803	49	33
16 9	76	1-	2103	152	134			

HK4 STRUCTURE FACTORS FOR BISMUTH MONOCHLORIDE

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
0	1734	1956	3 9	141	167-	6 13	136	75-	10 6	509	563-
2	196	82	3 10	217	265	6 14	171	168	10 7	148	132-
4	467	437-	3 11	83	84	6 15	162	138	10 9	117	104-
6	109	83	3 12	63	57-	6 16	62	33	10 10	61	12
8	365	431-	3 16	117	86-	7 2	257	220	10 11	82	78
12	113	133	3 17	82	36-	7 3	251	209	10 12	125	185-
14	153	140-	4 0	781	697-	7 4	181	151	10 15	53	47
18	98	102	4 1	154	83	7 5	471	456-	10 16	76	86
1 2	414	354	4 2	158	123-	7 6	226	169-	11 1	374	354
1 3	565	562	4 4	301	239	7 8	184	183-	11 2	417	454-
1 4	289	307-	4 5	254	185-	7 9	338	371	11 3	153	120-
1 5	181	122	4 6	71	74	7 11	144	149	11 5	282	272
1 6	154	115-	4 7	179	159	7 12	117	126-	11 6	122	84
1 7	177	162-	4 8	153	183	7 15	147	125-	11 7	96	117-
1 8	391	482	4 9	213	219	7 16	96	105	11 8	234	211-
1 9	225	216-	4 11	128	107-	7 17	36	39	11 9	418	447-
1 10	65	100-	4 12	87	81	8 1	109	43-	11 10	137	162
1 11	266	326-	4 13	94	66	8 2	316	327-	11 11	82	33-
1 12	147	153-	4 16	42	23-	8 3	253	187-	11 12	62	72
1 13	67	39	4 17	175	178-	8 5	246	161	11 14	61	114-
1 14	189	222	5 1	276	240-	8 6	340	376	11 15	86	79
1 15	135	109	5 2	142	121	8 8	155	196-	11 16	121	79
1 16	162	184-	5 3	201	151-	8 9	323	332-	12 0	623	648
1 17	108	98	5 4	190	135-	8 10	120	79-	12 1	155	157
1 18	118	108-	5 5	159	162-	8 16	130	82	12 2	144	157
2 2	434	319	5 6	285	287	8 17	173	219	12 3	143	140
2 3	198	178-	5 8	168	207-	9 1	315	325	12 4	261	252-
2 4	149	65-	5 9	390	459	9 2	247	191	12 5	262	245-
2 5	346	324	5 11	239	226	9 4	106	72-	12 8	91	84-
2 6	451	461-	5 12	231	234	9 5	121	117-	12 9	308	234
2 7	158	158	5 13	100	84-	9 6	217	216-	12 10	115	106-
2 8	159	137	5 14	118	115-	9 7	97	57-	12 12	96	87
2 9	109	69-	5 15	101	60-	9 8	71	49	12 13	126	162
2 10	124	100	5 16	79	41-	9 9	63	18-	12 14	85	94-
2 11	263	352	5 17	58	47-	9 10	137	143-	12 15	39	53
2 12	86	78-	6 0	475	482-	9 12	126	142-	12 16	104	86-
2 15	198	192-	6 1	115	23	9 13	63	65	13 1	284	270-
2 16	62	28-	6 2	404	388-	9 14	213	250	13 3	496	529
3 1	295	213	6 3	137	91	9 15	86	69	13 4	217	223-
3 2	310	206-	6 4	193	219	10 0	272	263-	13 6	390	299
3 3	531	568-	6 6	480	468	10 1	74	13	13 7	92	51-
3 4	264	230	6 8	117	114	10 2	544	618	13 8	151	194
3 5	394	419	6 9	202	208	10 3	177	118-	13 9	86	26
3 7	271	250	6 10	95	55-	10 4	243	223	13 11	175	171-
3 8	169	151	6 11	199	221-	10 5	102	29-	13 12	81	78

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
1313	69	36-	1704	157	154	2204	82	98
1314	97	134-	1705	84	24	2205	68	23
1315	99	101	1706	83	63-	2206	47	58-
14	190	214	1707	104	112	2207	70	59-
14 1	153	185-	1708	113	81-	2208	102	115-
14 2	141	130-	1709	145	93	2209	70	42-
14 3	66	95	1711	73	96	2301	125	144
14 4	96	147-	1714	44	23	2302	175	152-
14 5	330	349	1800	234	268-	2303	114	108-
14 6	113	126	1801	72	42-	2304	110	51
14 7	146	171-	1806	62	7-	2305	113	129
1410	147	146	1808	152	105	2306	70	57-
1411	242	252	1810	133	98-	2307	94	72
1412	68	11-	1811	177	163-	2308	56	75
1413	91	71-	1901	91	116	2309	156	183-
1414	84	84-	1906	74	2-	2400	120	91-
1415	131	98-	1907	163	76-	2401	154	171
15 1	220	250-	1908	207	247-	2402	126	116
15 2	109	42	1909	78	50	2403	74	63
15 3	163	110-	1910	85	79-	2404	76	46
15 5	152	96	1911	167	152	2405	149	110-
15 6	66	55-	1912	163	140	2406	131	106-
15 7	291	285	2000	248	232	2407	150	122
15 8	302	248	2001	143	128-	2408	35	75
1510	131	77	2002	64	11-	2501	79	105-
1511	91	82	2005	142	89-	2502	58	106-
1512	190	156-	2006	128	99	2503	52	60
1513	98	84	2008	168	163-	2504	84	74
1514	67	50	2009	62	23	2505	89	108
1515	112	105-	2010	101	88-	2506	124	124
16	327	391-	2011	178	140-	2601	38	44-
16 1	242	234	2101	60	45	2602	59	91-
16 2	154	84-	2102	121	123	2603	133	181
16 3	91	39	2103	261	287	2604	80	69-
16 4	130	57	2104	158	167-	2605	78	105
16 7	217	201	2105	188	205-	2606	83	90
16 8	161	143	2106	201	146-	2701	67	90-
16 9	120	128-	2107	116	96-	2702	85	109
1610	181	190	2108	84	60	2703	37	43-
1611	64	11-	2110	87	70-			
1612	64	51	2111	113	125-			
1614	40	32-	2200	151	130			
17 1	74	8	2201	159	139-			
17 2	72	68	2202	120	95			
17 3	318	273-	2203	137	132-			

HK5 STRUCTURE FACTORS FOR BISMUTH MONOCHLORIDE

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
3	554	384-	3 8	106	153	6 7	290	305	913	99	11
5	121	33-	3 9	108	82	6 8	145	111	914	57	43
9	130	134	311	227	218-	6 9	262	218-	10 1	201	188
11	117	206-	312	64	80-	610	237	277-	10 2	102	118-
13	364	533	313	137	159	612	221	272	10 3	235	253-
15	88	34-	314	67	20	614	186	192-	10 4	70	55
17	94	102-	315	41	29	615	227	191-	10 5	225	180-
1	321	319	316	77	104-	7	522	483-	10 6	95	79
1 1	354	375-	317	105	106	7 1	193	121-	10 7	185	96
1 2	537	397-	4 1	122	84-	7 2	264	191	10 8	319	321
1 3	407	277-	4 2	406	340	7 3	545	539	10 9	232	245-
1 4	96	46	4 4	200	156-	7 4	234	233	1010	79	103-
1 5	71	36-	4 5	181	184	7 6	171	154-	1011	264	327
1 6	189	143-	4 6	525	586-	7 7	144	166	1012	127	108-
1 7	134	37-	4 7	150	139-	7 9	168	164-	1014	72	56-
1 8	95	109-	4 8	273	295	710	190	234	1015	88	73
1 9	134	102-	4 9	123	139	711	122	152-	11	501	544-
110	106	129	410	220	188-	712	201	235-	11 1	158	152-
111	159	188	411	165	165-	713	127	148	11 2	207	192
112	51	55	412	187	197	714	158	155-	11 4	262	262-
113	46	41-	413	140	209-	715	177	149-	11 5	215	203
114	146	132	414	69	51	716	165	179	11 7	227	182-
115	108	64-	415	63	72	8 1	173	139-	11 8	61	83
117	146	174	416	56	17	8 2	310	241-	11 9	94	79-
2 1	136	78-	417	68	68-	8 3	468	473	1110	132	155-
2 2	527	405-	5	375	279	8 4	445	441	1111	212	219
2 3	110	73-	5 1	785	734-	8 5	451	419-	1112	202	169
2 4	276	170	5 2	151	96-	8 7	120	107-	1114	112	126
2 5	161	166	5 3	279	170	8 8	307	311	1115	99	134-
2 6	523	513-	5 4	262	188-	812	200	177-	12 1	164	172-
2 7	326	337-	5 5	148	131	813	155	133-	12 2	120	143-
2 8	287	277-	5 6	262	243	814	125	117-	12 4	210	197-
2 9	157	69	5 7	136	105-	815	52	44	12 5	206	206-
210	208	132	5 8	87	60	816	63	52	12 8	171	132-
212	251	302	5 9	127	84	9 1	422	357	12 9	102	88
214	66	66	510	226	245-	9 2	104	83	1210	89	99
215	57	30-	513	111	69-	9 3	455	534	1211	196	172
217	89	97	514	110	112-	9 4	201	183-	1212	143	117
3 1	209	103-	515	55	10	9 5	138	105-	1213	72	73-
3 2	100	18-	516	144	160-	9 6	243	218	1214	75	72-
3 3	332	274-	6 1	180	130	9 7	169	122	1215	101	108
3 4	255	158	6 2	129	52-	9 8	232	184-	13	334	295-
3 5	722	761-	6 3	217	187-	9 9	108	57-	13 1	132	150-
3 6	294	241-	6 4	179	146	910	197	207-	13 2	90	39
3 7	396	384	6 5	174	85	912	210	152	13 3	317	296-

H K	OBS	CALC	H K	OBS	CALC	H K	OBS	CALC
13 5	187	206-	17 7	63	25	23 1	91	122
13 7	203	229-	17 8	53	12	23 2	127	117-
13 9	188	191	1710	50	49-	23 4	141	124
1310	219	213	1711	67	47	23 5	114	129-
1311	58	25	1712	29	3	23 6	94	79-
1313	53	13-	1713	178	154-	23 7	42	4
1314	101	135-	18 2	357	467	23 8	74	81
1315	119	132	18 4	180	134-	24 1	48	26-
14 1	85	98-	18 5	257	214	24 2	85	109-
14 2	261	230	18 6	216	176	24 3	157	177-
14 3	86	79-	18 7	240	234-	24 4	72	62-
14 4	349	373-	18 8	65	76	24 5	46	59
14 6	111	99-	1810	120	73-	24 6	166	173-
14 7	242	320	1811	51	37-	24 7	51	54-
14 8	184	171-	1812	100	120-	25 1	144	137-
14 9	182	204-	19 1	147	162	25 2	74	75-
1410	57	37	19 2	74	67	25 3	26	7-
1411	48	59-	19 3	111	106	25 4	36	43-
1413	84	76	19 4	114	108	25 5	64	50-
1414	168	187	19 5	84	90			
15	263	273	19 6	231	205-			
15 1	261	227	19 9	140	127			
15 3	382	404-	1911	121	132-			
15 4	183	167-	1912	67	61-			
15 5	154	135-	20 1	167	156			
15 6	133	106	20 3	178	170-			
15 7	215	169	20 6	174	196			
1512	121	89-	20 8	53	72-			
1514	79	61-	2010	110	107			
16 1	66	93-	2011	108	101-			
16 2	121	127-	21	239	234			
16 3	139	146	21 2	308	284-			
16 4	299	337	21 3	81	62			
16 5	132	134	21 4	84	73			
16 8	328	408-	21 5	138	103			
16 9	78	59-	21 7	54	50-			
1610	156	163	21 8	174	151-			
1611	177	149-	2110	44	24			
1612	62	49-	22 1	72	39-			
1613	61	99-	22 2	179	158-			
17	151	111	22 5	130	133-			
17 1	89	82	22 7	146	147-			
17 3	202	213-	22 8	85	67			
17 5	280	323	22 9	196	211			
17 6	52	77-	23	179	194-			