THE CRYSTAL STRUCTURE OF SELENOUREA

THE CRYSTAL STRUCTURE OF SELENOUREA
AT 20°C AND AT -100°C.

By

JOHN STEWART RUTHERFORD, B.Sc.

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy.

McMaster University
October 1967.

DOCTOR OF PHILOSOPHY (1967)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario.

TITLE: The Crystal Structure of Selenourea at 20°C and at -100°C.

AUTHOR: John Stewart Rutherford, B.Sc. (Glasgow University).

SUPERVISOR: Professor C.Calvo.

NUMBER OF PAGES: vii, 97

SCOPE AND CONTENTS: The trigonal form of selenourea has been examined by X-ray crystallographic methods both at room temperature and at a lower temperature (-100°C). The lattice parameters of earlier workers have been refined and the space group assignment, which requires nine crystallographically distinct $SeC(NH_2)_2$ molecules, confirmed. The crystal structure was solved using a novel Patterson technique and differences Fourier syntheses, and was refined by least squares using three-dimensional data obtained at -100°C. Both the molecular dimensions and the crystal structure found are compared to other members of the urea series, and the similarity of the crystal structure to the urea- and thiourea-hydrocarbon complexes discussed. Evidence is presented of N-H...Se hydrogen bonds, supporting their recent discovery in chemically related compounds.

ACKNOWLEDGEMENTS.

I would like to express my gratitude to the following persons and organisations.

Professor C.Calvo, whose supervision was an ideal blend of sound advice and encouragement to pursue my own ideas.

The very many members of the Crystallography Group who provided computer programs and helpful advice, without either of which this research would not have borne fruit.

Canadian Industries Limited and the National Research Council of Canada, who provided personal financial support.

TABLE OF CONTENTS.

LIST OF ILLUSTRATIONS.

LIST OF TABLES.

CHAPTER I

INTRODUCTION

The crystal structure of selenourea, $SeC(NH_2)_2$, has been studied by single crystal X-ray diffraction techniques at room temperature and -100°C. Through this work, we intended to gain information on the structure of the selenourea molecule, the packing of these simple molecules in the solid state, and as to the existence of N-H...Se hydrogen bonds. The study was also concerned with the possibility of ferroelectricity in this molecular crystal. The structure found will be compared to those of the chemical analogues urea, $OC(NH_2)_2$, and thiourea, $SC(NH_2)_2$, and to their crystal complexes with hydrocarbons, with particular reference to the packing and degree of hydrogen bonding in these structures.

Selenourea was first prepared by Verneuil (1886) by reaction of hydrogen selenide with an aqueous solution of cyanamide,

$$H_2Se + H_2NCN \rightarrow SeC(NH_2)_2,$$

but until recently few workers have made any consistent study of its physical properties. There is not even agreement in the literature on the melting point, the usual criterion of purity for molecular solids. A number of reported values are:-

Recrystallisation From	Melting Point (°C)	Reference
Water	200 (dec.)	Verneuil (1886)
Water	213	Backer & Bos (1943)
Ethanol	210-211 (dec.)	Mautner (1956)
Water	235 (dec.)	Hope (1964)

The crystal structures of urea (Hendricks, 1928) and thiourea (Wyckoff and Corey, 1932) were among the earliest of molecular compounds to be solved. The urea structure, which has since been confirmed by both electron (Lobachev and Vainshtein, 1961) and neutron diffraction (Worsham, Levy and Peterson, 1957), contains two molecules in a tetragonal unit cell of space group D_{4d}^{3}-$P\bar{4}2m$ with $a = 5.661$Å, $c = 4.712$Å. The structure is illustrated in Figure I-1. The oxygen atom of each molecule is linked, by hydrogen bonds of length 3.0Å, to two nitrogen atoms on neighbouring molecules related by the $\bar{4}$ axis, and also to the two nitrogen atoms of the molecule related by the translations along this axis. This open framework of hydrogen bonds prevents other contacts between the urea molecules. The most recent X-ray studies are due to Sklar, Senko and Post (1961) and Caron and Donohue (1964). The former is of peculiar relevance to the

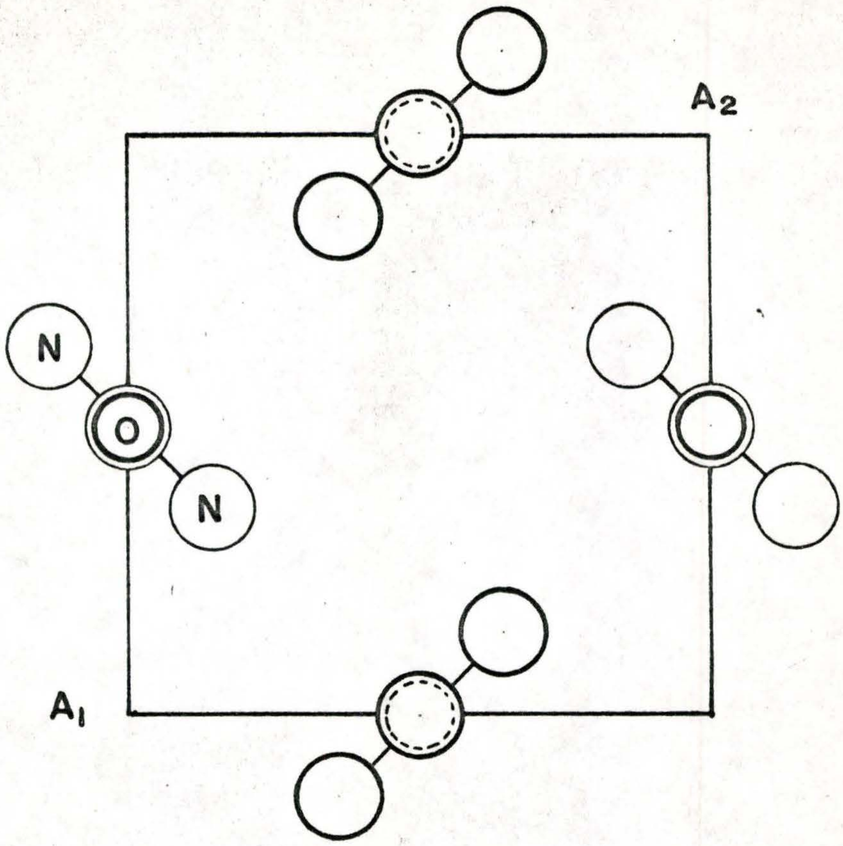


Figure I-1

The crystal structure of urea projected on (001).

present work, in being carried out at two temperatures, -140°C and 28°C.

Recent accurate X-ray determinations of the room temperature structure of thiourea have been carried out by Kunchur and Truter (1958), Zvonkova, Krivnov and Khvatkina (1966) and Truter (1967). The conclusions drawn are in agreement with an electron diffraction study by Dvoryankin and Vainshtein (1958). The structure involves four molecules in an orthorhombic cell, of space group D_{2h}^{16}-Pnma, and is illustrated in Figure I-2. The thiourea molecule has a plane of symmetry passing through the carbon and sulphur atoms, requiring the nitrogen atoms to be equivalent. The nitrogen atoms are found to be coplanar with the carbon and sulphur atoms, although this is not required by the space group symmetry.

Solomon (1957) reported that thiourea was ferroelectric at low temperatures, and Goldsmith and White (1958) showed that this results from small relative displacements of the molecules as a whole in a low temperature phase, stable below 169°K, of space group C_{2v}^{2}-$P2_1ma$, where the asymmetric unit is doubled in size. These displacements occur in either of two possible ways, which result in diametrically opposite directions for the residual dipole moment in this non-centrosymmetric structure. Since these displacements from the high temperature structure are small, the two forms have

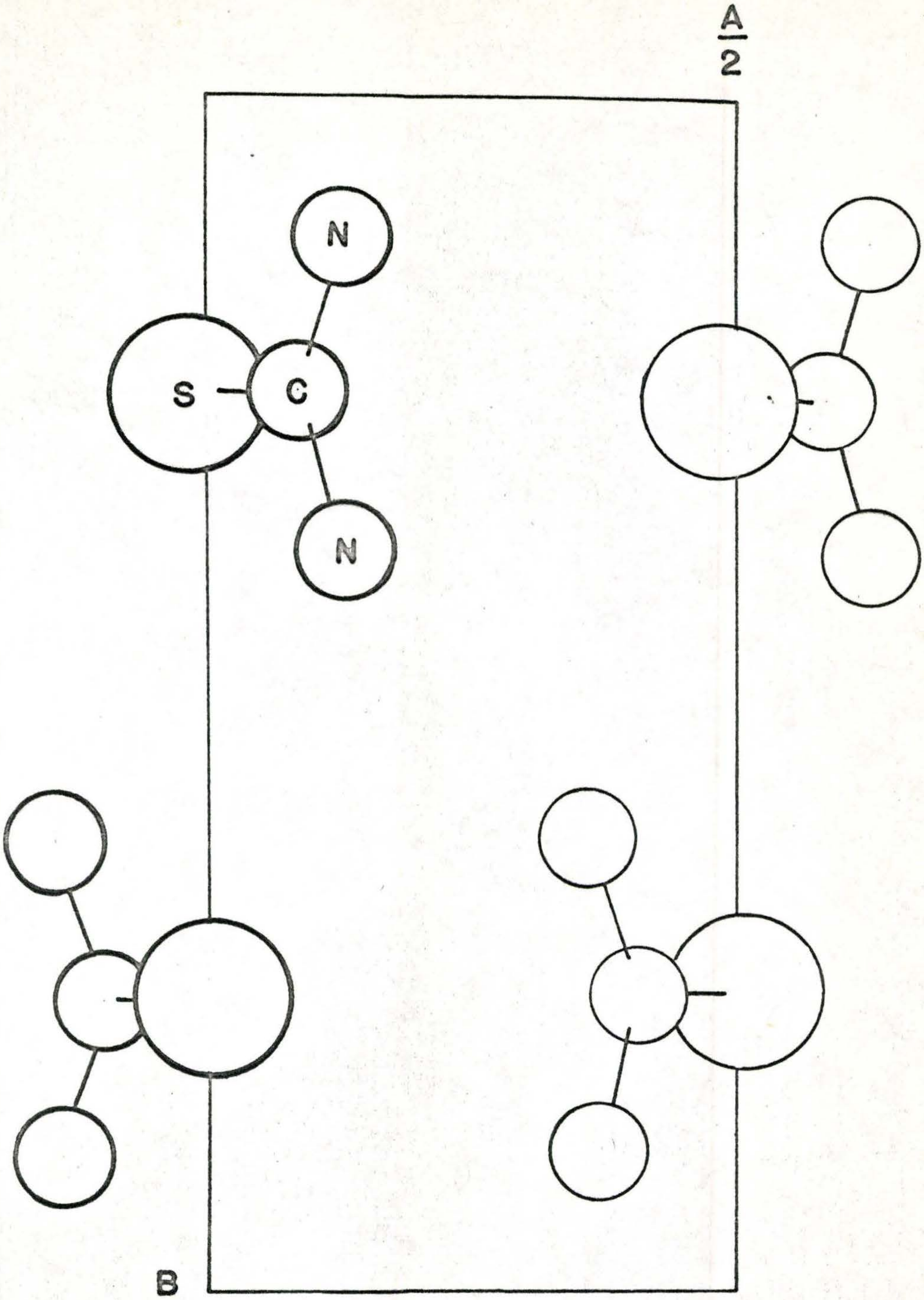


Figure I-2

The crystal structure of thiourea projected on (001).

only a small barrier to interconversion, which can be overcome by the application of an electric field of the correct polarity. Such an electric field will convert the crystal into the form with reversed moment; this phenomenon is called ferroelectric 'switching'. Again this low temperature structure has been confirmed by electron diffraction (Dvoryankin and Vainshtein, 1961) which in addition reveals the hydrogen bonding characteristics.

Kitaigorodskii (1961, 1965) is of the opinion that the determining factor in the crystal structure of organic compounds is steric, that is, the intermolecular interactions can be approximated as those arising from non-interpenetrable molecules. This 'hard molecule' model is in fact a good approximation from the point of view of lattice energy, since intermolecular forces can be shown to be not significantly affected by crystal fields in molecular crystals. Some examples substantiating this will be presented in the Discussion. The minimum free energy of the crystal then arises from the highest packing density, since the lattice energy is determined by the number of intermolecular contacts giving rise to the non-directional dispersion forces, commonly called van der Waals forces. What Kitaigorodskii has done is to derive a list of space groups which are likely to result in high packing density, through consideration of the effects of the various symmetry elements involved on a molecule of arbitrary shape.

These predictions are well borne out in practice. Dipolar interactions have little effect on this scheme, since they appear only to single out one particular free energy minimum from several available on purely steric grounds. The same is usually true of hydrogen bonds, despite their directed nature and the fact that they are found in practice to be saturated, that is, all available groups N-H and O-H are used in hydrogen bonding. However deviations from close-packing, due to the directional requirements of strong hydrogen bonds, do sometimes occur; this is well illustrated by comparing the structures of urea and thiourea.

With regard to urea, Kitaigorodskii points out that the structure is relatively 'loose' compared with the packing in most organic crystals, and attributes this to the steric requirements of the large number of hydrogen bonds involved. He also shows that thiourea would suffer from further large losses in packing density if it assumed the urea structure; thus the structure found for thiourea is of lower symmetry, but higher packing density, and is one of those theoretically predicted by Kitaigorodskii for the close-packing of organic molecules.

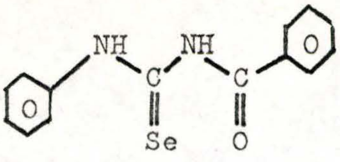
Urea and thiourea form inclusion compounds with certain hydrocarbons. The structure of the crystalline compounds formed by urea with straight-chain aliphatic hydrocarbons was elucidated by Smith (1952). The space group is $C6_12$ or the enantiomorphous $C6_52$. The unit cell contains six urea molecules, the lattice constants being a = 8.230(4)Å,[*] c = 11.005(5)Å. These urea molecules form a honeycomb structure by hydrogen bonding among themselves, leaving six-sided channels which contain the hydrocarbon molecules. The packing density in these crystals is greater than for either component alone which is further evidence in favour of Kitaigorodskii's principles.

A completely analagous phenomenon was also found for thiourea; in this case the structure determination is due to Lenné (1954). The basic structure has a similar honeycomb form, but the symmetry is reduced, the space group now being the rhombohedral R$\bar{3}$c. The unit cell has the dimensions a = 15.8Å, c = 12.5Å, contains 18 molecules of thiourea, and involves three six-sided channels, which are now large enough to contain cyclic hydrocarbons such as cyclohexane.

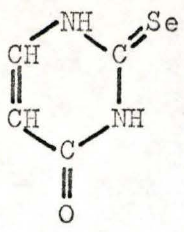
Recently three accurate crystal structure determinations of substituted selenoureas have been completed, phenylbenzoylselenourea (I) by Hope (1965), 2-selenouracil (II) by Tsernoglou (1966) and 2:4-diselenouracil (III) by Shefter, James and Mautner (1966).

---

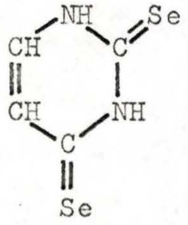
[*] Throughout this thesis errors (standard deviations where least squares is involved) will be designated by including the error in the final digit(s) in parentheses, e.g. 8.230(4)Å is equivalent to 8.230±0.004Å.



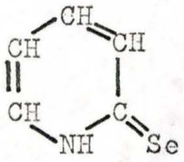
I.



II.



III.



IV.

All of these studies found the selenourea moiety, save possibly for the hydrogen atoms, to have the planar form found for the other members of the series, with Se-C-N and N-C-N angles near 120°. Some interatomic distances found are listed in Table I-1A. It will be shown below that these are in keeping with predictions based on the other analogues.

These three studies further produced all the crystallographic evidence to date for hydrogen bonds N-H...Se. The lengths of these hydrogen bonds are also listed in Table I-1A. For compounds II and III the interpretation is strengthened by the determination of the corresponding sulphur compounds, 2-thiouracil (Tsernoglou, 1966) and 2:4-dithiouracil (Shefter and Mautner, 1967). For example the N-H...Se distance in 2-thiouracil is 3.32Å, close

TABLE I-1

Some bond lengths and angles in compounds related to selenourea.

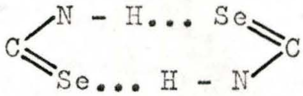
A. Substituted selenoureas.

Atoms.	Distance (Å).	Compounds.
C-Se	1.81	I
	1.84	II
C-N	1.32	I
	1.40	
	1.34	II
	1.34	
N-H...Se	3.83	I
	3.42	II
	3.47	III
	3.75	III

B. Urea and thiourea.

	C-X(Å)	C-N(Å)	X-C-N(°)	N-C-N(°)	Reference.
X=O	1.262(3)	1.341(3)	120.9(2)	118.2(2)	Sklar, Senko & Post (1961)
	1.276(8)	1.356(7)	120.5(6)	119.0(3)	Caron and Donohue (1964)
X=S	1.75	1.34	121	118	Goldsmith and White (1959)
	1.73	1.34	121	118	
	1.720(9)	1.340(6)	120.5(5)	119.0(5)	Truter (1967)

to the value of 3.30Å found in trimethylenethiourea (Diaz and Truter, 1964). For all three compounds two molecules are linked across a centre of symmetry by these hydrogen bonds, to form the grouping



The existence of similarly hydrogen bonded dimers has been deduced for 2-pyridselenone (IV) in solution by Krackov, Lee and Mautner (1965) on the basis of dipole moment and molecular weight measurements.

The urea series $XC(NH_2)_2$ have been the subject of a large amount of interest, as far as accurate molecular dimensions are concerned, since the system appears to exhibit electronic delocalisation, which increases the bond order of the C-N bonds and decreases the bond order of the C-X bond. This delocalisation also leads to hydrogen positions coplanar with the rest of the molecule. Typical bond lengths and angles found in this series are given in Table I-1B.

The first solid state study reported for selenourea was that of Mikhailov, Lundin, Gabuda and Aleksandrov (1961), who applied nuclear magnetic resonance techniques to powdered samples. They interpreted their results, on the basis of a similar molecular structure to thiourea, as indicating a distance of 1.75Å between protons on the same NH_2 group. This is similar to urea and thiourea. They also found that there is intermittent rotation of the molecule about the C-Se axis at temperatures above 130°K, and, by consideration of the variation of the second moment with temperature, showed that the barrier to the rotation is around 6 kilocalories per mole, which can be compared with values of 12.7 kilocalories per mole for urea and 9 kilocalories per mole for thiourea, both determined by the same technique. It is unfortunate that there is no crystal data on the samples used by Mikhailov et al., in light of the subsequent reports by other workers of two separate crystalline modifications of selenourea.

Dvoryankin and Ruchkin (1962) reported an initial electron diffraction study of selenourea. The crystals, prepared by recrystallisation from ethanol-water solutions, were found to belong to the space group Pnma, with the lattice constants here compared to the high temperature form of thiourea, which belongs to the same space group.

	a(Å)	b(Å)	c(Å)	V(Å^3)	Z
Selenourea	6.48	8.75	7.04	399	4
Thiourea	7.65	8.53	5.52	361	4

This phase has not been confirmed by any of the subsequent

X-ray work.

Preliminary accounts of the unit cell dimensions and contents of a second modification have been given by Kondrashev and Andreeva (1963), Perez Rodriguez, Cubero and Lopez-Castro (1964), and Hope (1965), all using X-ray methods. Kondrashev and Andreeva studied single crystals grown from aqueous solution, and assigned them to one of the enantiomorphous pair of space groups $P3_1$, $P3_2$, on the basis of the systematic absences ($00\ell, \ell \neq 3n$) found in the diffraction pattern. Perez Rodriguez et al. found the crystal to have the same space group, but noted that careful examination of the intensities is required to eliminate the higher symmetry point groups D_3, C_{3v} and D_{3d}. Hope did not venture to assign a space group in his report. The unit cell contains 27 molecules, and is very similar in dimensions to those of the urea- and thiourea- hydrocarbon inclusion compounds which contain 18 $XC(NH_2)_2$ molecules. The urea compound requires a transformation to a triply-primitive cell for comparison.

	a(Å)	c(Å)
Selenourea (Perez Rodriguez et al.)	15.34	12.99
Thiourea/cyclohexane	15.8	12.5
Urea/n-hexadecane	14.3	11.0

This suggests that perhaps 18 molecules per unit cell are involved in a similar honeycomb structure, while the remaining nine are distributed in the channels, three to each. Kondrashev and Andreeva further report that this is born out by the hk0 Patterson function, which illustrates the position of the 18 selenium atoms of the honeycomb structure.

The study reported here was commenced in 1962. As the work described above became available, it became clear not only that there was, for various reasons, a great deal of interest in the crystal structure of selenourea, but that some duplication of effort might ensue as a result. In particular, Lopez-Castro (1965) confirmed her intention of carrying out a complete room temperature study. At this point it was decided to conduct a parallel low temperature structure determination; -100°C was chosen as a convenient temperature considering the apparatus available.

The rationale for low temperature crystal structure determination is the following. The diffraction experiment does not record an atom in its equilibrium position, but a distribution of atoms displaced from their equilibrium positions by thermal motion. In fact the variation in intensity with temperature for a monatomic isotropic crystal involved the factor $e^{-2B(\sin\theta/\lambda)^2}$, where $B = 8\pi^2\overline{\mu^2}$, and $\overline{\mu^2}$ is the mean square displacement of the atom from its equilibrium position. $\overline{\mu^2}$ increases with increasing temperature, the variation being close to linear except at very low temperatures (Lonsdale and El Sayed, 1965), and makes it more difficult to determine the true equilibrium position, and hence chemically important bond lengths. One way of looking at this effect is to note that the intensities decrease with increasing temperature, especially for large values of $(\sin\theta/\lambda)$, this results in a smearing out of atoms in electron density maps, because of the decrease in magnitude of these higher order Fourier coefficients. This has been illustrated by Burbank (1953), using the expressions and notation of Cruikshank (1949). The standard deviation $\sigma(x)$ in a co-ordinate derived from such electron density maps, is given by

$$\sigma(x) = \frac{\sigma(A_n)}{A_{nn}} \tag{I-1}$$

where

$$\sigma(A_n) = \frac{2\pi}{aV}\left\{\sum_{hk\ell} h^2(\Delta F_{hk\ell})^2\right\}^{1/2}$$

and

$$A_{nn} = -\frac{\delta^2\rho}{\delta x^2}$$

$\sigma(A_n)$ is simply proportional to the root mean square difference between the observed and calculated structure factors, $\Delta F_{hk\ell}$, properly weighted with respect to the co-ordinate x. Thus it depends primarily on the accuracy of the data. A_{nn}, however, is the curvature of the electron density at the peak position, and Burbank calculated this for various elements and values of B. For example, for carbon

B	0	2	4
A_{nn} (electrons/Å^5)	-264	-119	-58

The latter two values of B correspond roughly to 150°K and 300°K for many molecular compounds; thus we should hope to obtain more accurate atomic positions, and hence interatomic distances, by a factor of about 2 from work at -100°C.

Cruickshank (1960) himself has discussed the accuracy required in intensity measurement to gain sufficient accuracy in interatomic distances, and stresses the importance of low temperature work, suggesting that all molecular crystal work should be carried out at 100°K (-173°C) or lower. In addition to the greater resolution described above, he points out that errors can arise in the apparent equilibrium positions at high temperatures, caused by both molecular libration and anharmonicity in the lattice vibrations. It is difficult to correct for these effects without knowing the detailed nature of the crystal vibrations. This plea has gone unheeded since in practice a very small proportion of crystal structures are determined at low temperatures.

CHAPTER II

EXPERIMENTAL

General remarks.

X-ray diffraction is by now a very well established technique for the determination of the atomic arrangements in crystals. The majority of experimental apparatus and techniques, and of theoretical results, used in this study have been known for several decades, are in worldwide everyday use, and are well described in a number of standard texts (Buerger, 1942, 1960, Lipson and Cochran, 1967, etc.) I therefore feel it unnecessary to attempt a prolonged description of such methods here, and prefer to limit more detailed description to techniques which are either new or unusual.

The low temperature apparatus.

The low temperature work used the Nonius Weissenberg camera with low temperature attachment. This consists of an insulated tube, which passes down within, and concentric with, the layer line screen to a position just short of the crystal;

a controlled stream of cold nitrogen is passed through this tube and over the crystal. The nitrogen then passes out again through the open end of the layer line screen. The temperature is monitored by means of a copper-constantan thermocouple at the end of the tube nearest the crystal. To maintain the film at room temperature and to prevent frosting, the tube is surrounded by a heating coil, and the layer line slit is sealed with cellophane tape. With these precautions the cooling of the actual film holder amounted to only a few degrees, sufficient to cause condensation only on the most humid days. The cold nitrogen stream is produced in our apparatus by boiling liquid nitrogen by means of electrical heating. Temperatures in the range -150°C to room temperature can be readily achieved and maintained with this apparatus, although the lowest temperatures need careful monitoring and a prodigal expenditure of liquid nitrogen.

The determination of lattice parameters.

On crystallisation from water, selenourea forms trigonal prisms, the prominent forms being {001}, $\{00\bar{1}\}$ and {100}. The identity of the last named prism faces was found by X-ray diffraction, which also showed the Laue symmetry C_{3i}. Since the only systematic absences observed are 00ℓ, $\ell \neq 3n$, this leads immediately to the enantiomorphous pair of space groups $P3_1$ and $P3_2$ (C_3^2 and C_3^3). No space group with these extinctions occurs in the centrosymmetric point group C_{3i}.

The Bragg equation

$$n\lambda = 2d \sin \theta \qquad \text{(II-1)}$$

relates the spacing $d_{hk\ell}$ between succesive planes of Miller indices $hk\ell$ in the crystal lattice. We can therefore, knowing the wavelength of the radiation used, measure the dimensions of the unit cell.

The lattice parameters of selenourea were measured at 20°C by superimposing the diffraction pattern of a single crystal of rutile (the tetragonal modification of TiO_2) on an $h0\ell$ Weissenberg photograph for selenourea, in both cases using CoKα radiation.* The lattice parameters of rutile have been accurately determined as a = 4.5929(5)Å, c = 2.9591(3)Å by Cromer and

---

*The x-radiations used in this study, with their wavelengths, as listed in International Tables for X-ray Crystallography, and corresponding Kß filters, were :-

Radiation	α_1	α_2	Filter
CoKα	1.78892	1.79278	Fe
CuKα	1.54051	1.54433	Ni
MoKα	0.70926	0.713543	Zr

Herrington (1955). These values were used to correct the selenourea measurements for camera radius and film shrinkage; the rutile measurements were all consistent with an effective camera radius of 2.848 cm. The corrected values of the angles, θ, for 12 h0ℓ reflections were used to determine the lattice parameters by least squares, using the values of Perez Rodriguez et al. as a starting point, and the FORTRAN program DESLS (Robertson,1966) on the I.B.M. 7040 computer, which was used for all computations. The observed angles are tabulated (Table II-1A), together with those calculated from the lattice parameters found by least squares, namely a = 15.285(5)Å, c = 13.007(5)Å at 20°C.

These values correspond to a unit cell whose volume is 2631Å^3. If we assume that the cell contains 27 molecules of the formula $SeC(NH_2)_2$, (formula weight 123.01),then the individual molecular volume is 97.4Å^3, and the calculated density is 2.09. Literature values are 2.06, 2.09 (Kondrashev and Andreeva), and 2.1 (Perez Rodriguez et al.). Since the space group $P3_1$ contains only 3-fold positions we have further reason to rule out other possibilities. Thus we have nine crystallographically distinct molecules in the unit cell.

If the diffraction patterns at two temperatures of a single crystal are superimposed on one film, and provided the structure and orientation are preserved in going from one temperature to the other, it is possible to determine with a very

TABLE II-1.

Observed and calculated diffraction angles in the lattice parameter determinations for selenourea.

A. Room temperature.

hkℓ	θ(Obs.) degrees.	θ(Calc.) degrees.
300	11.72	11.70
003	11.92	11.91
303	16.83	16.82
600	23.96	23.94
006	24.44	24.39
603	27.10	27.08
306	27.40	27.39
307	31.49	31.51
900	37.50	37.49
009	38.24	38.27
607	39.05	39.04
903	39.94	39.99

B. Low temperature.

hkℓ(*)	$\Delta\theta$(Obs.) degrees.	$\Delta\theta$(Calc.) degrees.
3,3,14	0.48	0.49
6,6,11	0.58	0.56
1,1,15	0.48	0.51
990	0.70	0.70
991	0.65	0.71
2,2,15	0.58	0.57
5,5,13	0.70	0.65
7,7,10	0.68	0.71
993	0.80	0.79
888	0.80	0.82
994	0.90	0.94

(*) In order of increasing θ.

high degree of accuracy the changes in lattice parameters over the temperature range in question. This arises because this relative measurement of the Bragg angle not only automatically corrects for the effects of film shrinkage and camera radius mentioned above, but also, since the same crystal is used throughout, for errors resulting from crystal eccentricity and absorption.

This technique was applied to selenourea, using the Nonius Weissenberg camera. The crystal was oriented so that the $hh\ell$ reciprocal lattice zone was recorded, and exposures were taken at 20°C and -100°C using CuKα radiation with the camera displaced slightly laterally between exposures. The relative spacing of the α_1, α_2 doublets at both temperatures were measured for 11 reflections, and these were used to determine the change in lattice parameters again using the DESLS program. These were found to be 0.084(1)Å in $\underline{a}$ and 0.057(1)Å in $\underline{c}$, corresponding to coefficients of thermal expansion averaged over this temperature range of $\alpha_a = 46 \times 10^{-6}/^{\circ}C$ and $\alpha_c = 36 \times 10^{-6}/^{\circ}C$. Since the changes are known much more accurately than the parameters themselves, we can say that the unit cell dimensions at -100°C are $\underline{a} = 15.201(5)$Å, $\underline{c} = 12.950(5)$Å. The observed and calculated changes in angle, averaged for each doublet, are tabulated in Table II-1B.

The measurement of intensity data.

All intensity data were measured by photographic techniques, using single crystal cameras based on the Weissenberg (1924) or Buerger precession (1944) motions. The measured intensities were assigned standard deviations assuming a constant relative error of 20%, or an error equal to the minimum observable intensity on that particular set of films, whichever was greater. These standard deviations were later used in weighting observations in least squares refinements. As a weighting scheme, this is as simple to apply as that suggested by Hughes (1941), is almost identical in effect, and has the added advantages of taking account of local variations in F_{min}, and of allowing weighted averaging of equivalent structure factors. Absorption corrections were then made as detailed below, and Lorentz and polarisation corrections were applied using the FORTRAN programs WEILPC (Weissenberg) and PRELPC (precession) written in this laboratory. All data were finally converted to structure factors with each layer scaled independently.

The data used for the room temperature study consisted of 3 reciprocal lattice zones, each gathered by a different photographic technique. All other data collected at room temperature were found to be useless for intensity measurement because of the use of twinned crystals. The nature of the twinning will be described in the Discussion.

The $h0\ell$ data were collected on the Supper Weissenberg camera, using Cu-Kα radiation, and the multiple film technique (Robertson, 1943) with Ilford Ilfex X-ray film (transmission for CuKα radiation 1/2.7). Since the crystal used was extremely small (less than 10^{-7}c.c.) no absorption correction was made to this data. The intensity measurements for the hk0 zone used a somewhat larger crystal, yet still small enough to avoid twinning effects. This time the precession camera was used, along with MoKα radiation, for which the absorption factor for selenourea is 100cm.^{-1}. On the precession camera timed exposures were used rather than the multiple film technique. Approximate absorption corrections were applied to this data by assuming the crystal to be a sphere of radius 0.02cm. ($\mu R = 2$) and interpolating between the values in the table in International Tables for X-ray Crystallography.

For the $hh\ell$ data a larger crystal could be used, since for this projection the twinning does not interfere. This allowed the use of the integrating precession camera (Nordman, Patterson, Weldon and Supper, 1955), and the measurement of the intensities with a Leeds and Northrup Gl microdensitometer. The crystal used was a thin plate, oriented so that the surface of the plate was parallel to the film. Again a series of timed exposures were taken. No absorption correction was applied to this data.

The low temperature data were all taken on the Nonius

Weissenberg camera, using CuKα radiation and equi-inclination geometry (Buerger 1942). The crystals used were all prisms of volume less than 5 X 10^{-7}c.c., since it had been found during the room temperature study that crystals of volume 10^{-5}c.c. or greater were frequently twinned. The small crystals made the exposure time required for integrated photographs inconveniently long, considering the temperature had to be monitored at about hourly intervals, and the duration of a 25 litre can of liquid nitrogen was 10 - 12 hours. As it was, the low temperature study was accomplished entirely by non-integrated multiple film exposures, and exposure times of 10 - 12 hours were barely adequate. The dimensions of the crystals used (length and mean width) and the layers collected with each are listed in Table II-2.

It was found convenient to index the h,h+n,ℓ data on the basis of the orthohexagonal cell, and to compute the absorption, Lorentz and polarisation corrections in this form, before transforming to the primitive cell.

The data were corrected for absorption by assuming that the crystals were cylinders (hkn data) or rectangular prisms (hnℓ and h,h+n,ℓ data) of the dimensions stated, and ignoring edge effects. In this approximation the path length to and from any point in the crystal for a reflection of radial co-ordinate ξ[*] (which equals

---

[*] This co-ordinate system and nomenclature is that described in Buerger (1942).

TABLE II-2.

Details of the layer line data used in the low temperature study.

Layer Indices	Crystal Dimensions (cm.X10^3)		Number of Reflections			Weighted R Factor on Merging.
	Length	Diameter	Observed	Unobserved	Total	
hk0	15	3	107	57	164	0.178
hk1	20	4	85	243	328	0.209
hk2	20	2	97	231	328	0.088
hk3	20	2	129	97	226	0.128
h0ℓ	18	5	143	275	418	0.171
h1ℓ	18	5	146	532	678	0.208
h2ℓ	18	5	340	151	491	0.160
hhℓ	20	4	130	100	230	0.171
h,h+1,ℓ	20	4	289	149	438	0.167
h,h+2,ℓ	20	4	336	113	449	0.157
Total			1802	1948	3750	0.159

2 sin θ for zero layer) and angular co-ordinate $\bar{\varphi}$, measured at equi-inclination angle ν, is simply sec ν times the path length for the zero level reflection of co-ordinates ξ and $\bar{\varphi}$. The cylindrical absorption corrections were interpolated from the values given in International Tables for X-ray Crystallography, using $\mu R \sec \nu$ where appropriate. The correction for the rectangular prism was made using the Albrecht (1939) method, programmed on the I.B.M. 7040 computer. The program computed for each reflection the attenuation of the beam diffracted by 100 points (distributed on a regular 10 X 10 grid) within the crystal, and corrected the observed intensity by multiplying by the inverse of the mean attenuation.

The solution of the structure.

The intensity of diffraction for any particular reflection, with which we can associate the reciprocal lattice point $\underline{H}$, for which the momentum transfer on scattering is given by the Laue equation

$$\underline{k}_o - \underline{k} = 2\pi\underline{H} \qquad \text{(II-2)}$$

is proportional to the square of the structure factor $F_{\underline{H}}$. The structure factor is related to the electron density ρ at a point

$\underline{r}$ within the unit cell by the expression

$$F_{\underline{H}} = \int \rho(\underline{r}) e^{2\pi i \underline{H}\cdot\underline{r}} d\underline{r} \qquad \text{(II-3)}$$

If we assume the electron density to be composed of N spherically symmetric atoms, and, ignoring temperature effects for the moment, we have

$$F_{\underline{H}} = \sum_{j=1}^{N} f_j(|\underline{H}|) e^{2\pi i \underline{H}\cdot\underline{r}_j} \qquad \text{(II-4)}$$

where f_j is called the atomic scattering factor. The structure factor and the electron density are the Fourier transforms of each other, that is we can evaluate the electron density, knowing the $F_{\underline{H}}$'s, as the Fourier series

$$\rho(\underline{r}) = \frac{1}{V} \sum_{\underline{H}} F_{\underline{H}} e^{-2\pi i \underline{H}\cdot\underline{r}} \qquad \text{(II-5)}$$

If we do not know the phases of the complex quantities $F_{\underline{H}}$, we can construct another series, the Patterson function

$$\begin{aligned} P(\underline{u}) &= \frac{1}{V} \sum_{\underline{H}} F_{\underline{H}} F_{\underline{H}}^{*} e^{-2\pi i \underline{H}\cdot\underline{u}} \\ &= \frac{1}{V} \sum_{\underline{H}} \sum_{j=1}^{N} \sum_{k=1}^{N} f_j f_k e^{2\pi i \underline{H}\cdot(\underline{r}_k - \underline{r}_j)} \, e^{-2\pi i \underline{H}\cdot\underline{u}} \qquad \text{(II-6)} \end{aligned}$$

This function then contains N^2 peaks, of magnitude $f_j f_k$, located at $\underline{r}_j-\underline{r}_k$ from the origin. If we can interpret the Patterson in terms of such a vector set (Buerger,1959) we have a solution for the crystal structure. We can then refine the parameters in our model to improve the agreement between our observed and calculated structure factors.

When we apply this technique to selenourea, we find that we can ignore interactions other than Se-Se, so that we have 27^2 vectors to locate and identify. We can reduce this number by ignoring origin peaks j=k, taking account of the centre of symmetry ($\underline{r}_k-\underline{r}_j$ must exist as well as $\underline{r}_j-\underline{r}_k$) and the 3-fold axis to 117 distinct peaks. Even then, this is a problem somewhat beyond the brute force approach.

However, a marked pattern of more intense reflections was noted on the films corresponding to the indices -h+k = 3n. In the h0ℓ zone, for example, the ratio of the most intense reflections of each class, I_{003}/I_{103}, is about 9. For the hk0 zone it is even higher. This implies a marked pseudosymmetry, a hexagonal subcell of dimensions one third of the true cell, having the same c-axis and the orientation shown in Figure II-1. This rotation about $\underline{c}$ involves the transformation matrix

$$T = \begin{pmatrix} 1/3 & -1/3 & 0 \\ 1/3 & 2/3 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \text{(II-7)}$$

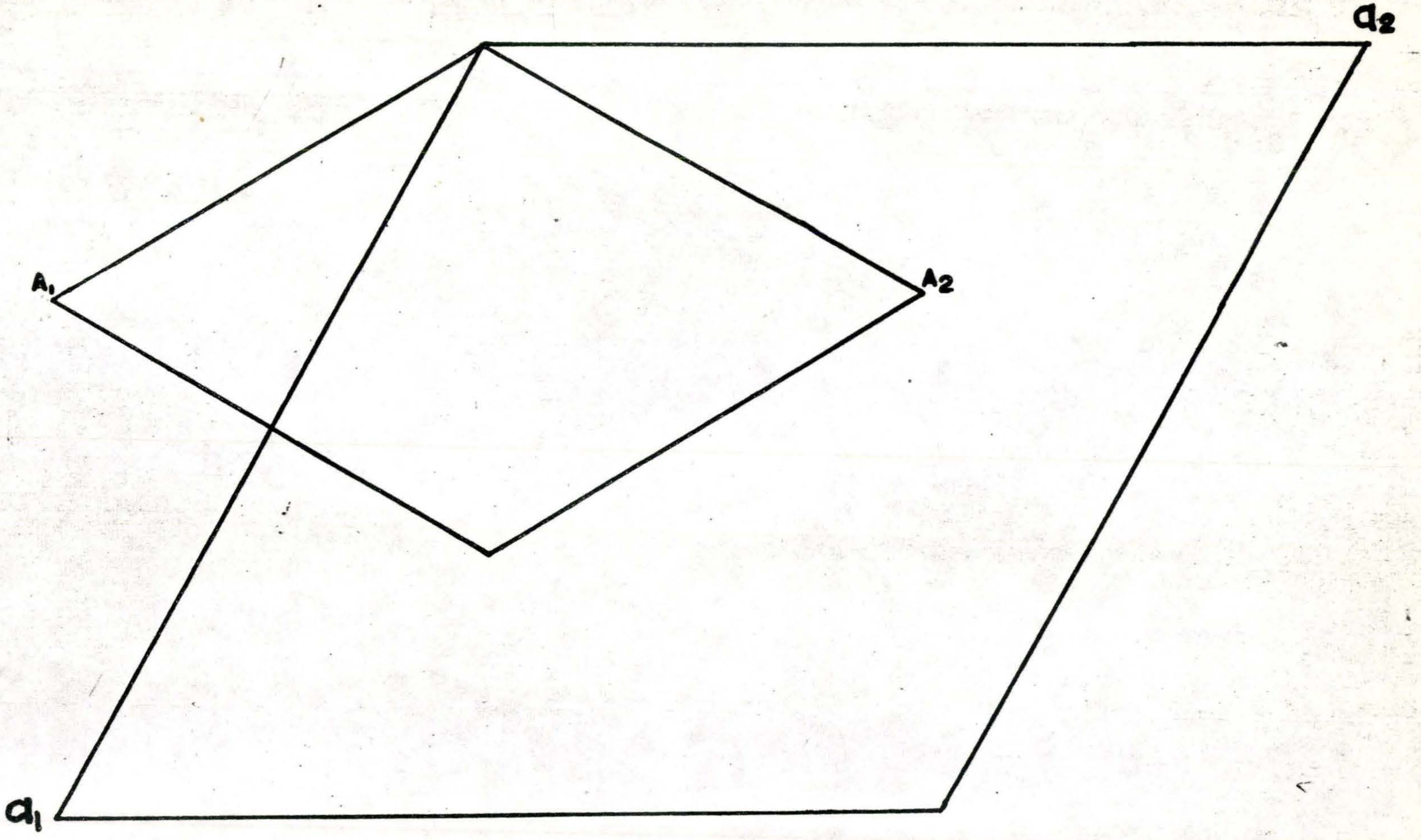


Figure II-1

The relationship in orientation and dimensions between the small pseudo-cell and the true unit cell.

where T is here quoted in the form with determinant 1/3, corresponding to the 3-fold decrease in cell volume. The transpose of the inverse matrix is

$$R = \begin{pmatrix} 2 & -1 & 0 \\ 1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

This governs the corresponding reciprocal lattice transformation, so that we have the relationships

$$A = Ta \qquad X = Rx$$

$$B = Rb \qquad H = Th$$

where a,b,x, and h are the real axes, reciprocal axes, real space co-ordinates and reciprocal space co-ordinates respectively for the superlattice, and their upper case equivalents the corresponding sublattice quantities.

Further, the layers hk0, hk1 and hk2 (although the latter two were not used for intensity measurements) showed a further pattern of intense spots, as well as the rule described above. These correspond to

$$-H+K+L = 3n$$

where HKL are the indices in terms of the small cell.

This implies that within the subcell there is an approximate rhombohedral centering, that is, there are equivalent atoms at the points (0,0,0), (2/3,1/3,1/3) and (1/3,2/3,2/3) in terms of the subcell. Applying

$$x = R^{-1}X$$

these become (0,0,0), (1/3,0,1/3) and (2/3,0,2/3).

Taken together with the translations corresponding to the subcell, we have the nine approximately equivalent positions

(0, 0, 0)	(1/3, 0, 1/3)	(2/3, 0, 2/3)
(2/3,1/3,0)	(0, 1/3,1/3)	(1/3,1/3,2/3)
(1/3,2/3,0)	(2/3,1/3,1/3)	(0, 2/3,2/3)

We can refine this approach still further, by attempting to solve the Patterson function within the small cell. This approach is justified in the following way. We assume that the superlattice involves a set of small displacements from an ideal sublattice structure. We then have, for an M-fold increase in the unit cell

$$F_{\underline{H}} = \sum_{j=1}^{N} \sum_{\ell=1}^{M} f_j e^{2\pi i \underline{H}\cdot(\underline{r}_j + \underline{\delta}_{j\ell} + \underline{\Delta}_{\ell})}$$

where $\underline{r}_j$ is the average position in the ideal cell of atom j, and

$\underline{\delta}_{j\ell}$ is its displacement from this position in the subcell ℓ, which we always assume small, and $\underline{\Delta}_\ell$ is the vector from the origin to the origin of subcell ℓ, that is, it is a sublattice translation. For sublattice reflections, we have

$$F_{\underline{H}} = \sum_{j=1}^{N} \sum_{\ell=1}^{M} f_j e^{2\pi i \underline{H}\cdot\underline{r}_j} \; e^{2\pi i \underline{H}\cdot\underline{\delta}_{j\ell}}$$

$$= \sum_{j=1}^{N} \sum_{\ell=1}^{M} f_j e^{2\pi i \underline{H}\cdot\underline{r}_j} \left(1+2\pi i\underline{H}\cdot\underline{\delta}_{j\ell}-\frac{4\pi^2}{2!}(\underline{H}\cdot\underline{\delta}_{j\ell})^2 \ldots\right)$$

$$\approx \sum_{j=1}^{N} \sum_{\ell=1}^{M} f_j e^{2\pi i \underline{H}\cdot\underline{r}_j} \left(1-2\pi^2(\underline{H}\cdot\underline{\delta}_{j\ell})^2\right) \qquad \text{(II-9)}$$

This implies that using the sublattice reflections, we can construct a Patterson function which we can attempt to solve for the ideal structure, since this approximates, especially for small $\underline{H}$

$$M \sum_{j=1}^{N} f_j e^{2\pi i \underline{H}\cdot\underline{r}_j}$$

To illustrate what sort of approximation this is, I shall introduce a special case, where only a doubling of the unit cell is involved. Then $\underline{\delta}_j, = \underline{\delta}_{j1} = -\underline{\delta}_{j2}$ and

$$F_{\underline{H}} = 2\sum_{j=1}^{N} f_j e^{2\pi i \underline{H}\cdot\underline{r}_j} \; \cos 2\pi(\underline{H}\cdot\underline{\delta}_j)$$

For the superlattice reflections, we have

$$F_{\underline{H}} = \sum_{j=1}^{N} \sum_{\ell=1}^{M} f_j e^{2\pi i \underline{H}\cdot(\underline{r}_j+\underline{\Delta}_\ell)} \left(1+2\pi i \underline{H}\cdot\underline{\delta}_{j\ell} - \frac{4\pi^2}{2!}(\underline{H}\cdot\underline{\delta}_{j\ell})^2 \ldots\right)$$

$$= \sum_{j=1}^{N} \sum_{\ell=1}^{M} f_j e^{2\pi i \underline{H}\cdot(\underline{r}_j+\underline{\Delta}_\ell)} \left(2\pi i \underline{H}\cdot\underline{\delta}_{j\ell} - \frac{4\pi^2}{2!}(\underline{H}\cdot\underline{\delta}_{j\ell})^2 \ldots\right)$$

$$\approx \sum_{j=1}^{N} \sum_{\ell=1}^{M} 2\pi i (\underline{H}\cdot\underline{\delta}_{j\ell}) f_j e^{2\pi i \underline{H}\cdot(\underline{r}_j+\underline{\Delta}_\ell)} \qquad \text{(II-10)}$$

For the special case above

$$F_{\underline{H}} = \sum_{j=1}^{N} f_j e^{2\pi i \underline{H}\cdot\underline{r}_j} \left\{ e^{2\pi i \underline{H}\cdot\underline{\delta}_j} - e^{-2\pi i \underline{H}\cdot\underline{\delta}_j} \right\}$$

$$= \sum_{j=1}^{N} 2i f_j e^{2\pi i \underline{H}\cdot\underline{r}_j} \sin 2\pi(\underline{H}\cdot\underline{\delta}_j)$$

Now, if we construct a Patterson using only the superlattice reflections we get

$$P(\underline{u}) = \frac{1}{V} \sum_{\underline{H}} F_{\underline{H}} F_{\underline{H}}^{*} e^{-2\pi i \underline{H}\cdot\underline{u}}$$

$$= \frac{1}{V} \sum_{\underline{H}} \sum_{j=1}^{N} \sum_{k=1}^{N} \sum_{\ell=1}^{M} \sum_{m=1}^{M} 4\pi^2 (\underline{H}\cdot\underline{\delta}_{j\ell})(\underline{H}\cdot\underline{\delta}_{km}) f_j f_k e^{2\pi i \underline{H}\cdot(\underline{r}_k+\underline{\Delta}_m-\underline{r}_j-\underline{\Delta}_\ell)}$$

$$e^{-2\pi i \underline{H}\cdot\underline{u}} \qquad \text{(II-11)}$$

which can be interpreted as a function with features at the points $\underline{r}_k-\underline{r}_j+\underline{\Delta}_m-\underline{\Delta}_\ell$, ($\underline{\Delta}_m-\underline{\Delta}_\ell$ being a subcell translation) whose magnitudes are proportional to $(\overline{\underline{H}.f_j\underline{\delta}_{j\ell}})(\overline{\underline{H}.f_k\underline{\delta}_{km}})$ where the bar represents an average over $\underline{H}$. The features on the normal Patterson at these points are of magnitude $f_j f_k$, so we can now find the value of $(\overline{\underline{H}.f_j\underline{\delta}_{j\ell}})(\overline{\underline{H}.f_k\underline{\delta}_{km}})$. This gives us the sign of the displacements of atoms $j\ell$ and km relative to each other, from which we may hope to solve the superlattice structure. By the way, the height of the origin peak here will be

$$\frac{1}{V}\sum_j\sum_\ell 4\pi^2(\overline{\underline{H}.f_j\underline{\delta}_{j\ell}})^2$$

that is, proportional to the weighted mean square displacement of all the atoms from the average structure.

The interpretation of the Patterson function for structures involving superlattices, using the two sets of reflections independently, has been suggested by Buerger (1959). His analysis, however, is unsuitable for the present case, since it is in terms of a 'complement structure' which consists of electron density added to the substructure. Mackay (1953) was the first to discuss superstructures in terms of displacements from an average structure; he found that the ratio between the average intensities of the two classes of reflections is given, for equal atoms,

$$R = 4\pi^2(\overline{\underline{H}.\underline{\delta}_j})^{2(*)}$$

(*) A more accurate result is $4\pi^2(\overline{\underline{H}.\underline{\delta}_j})^2/[1-4\pi^2(\overline{\underline{H}.\underline{\delta}_j})^2]$

or assuming random displacements

$$R = 2\pi^2 d^{*2} \delta^2 \qquad \text{(II-12)}$$

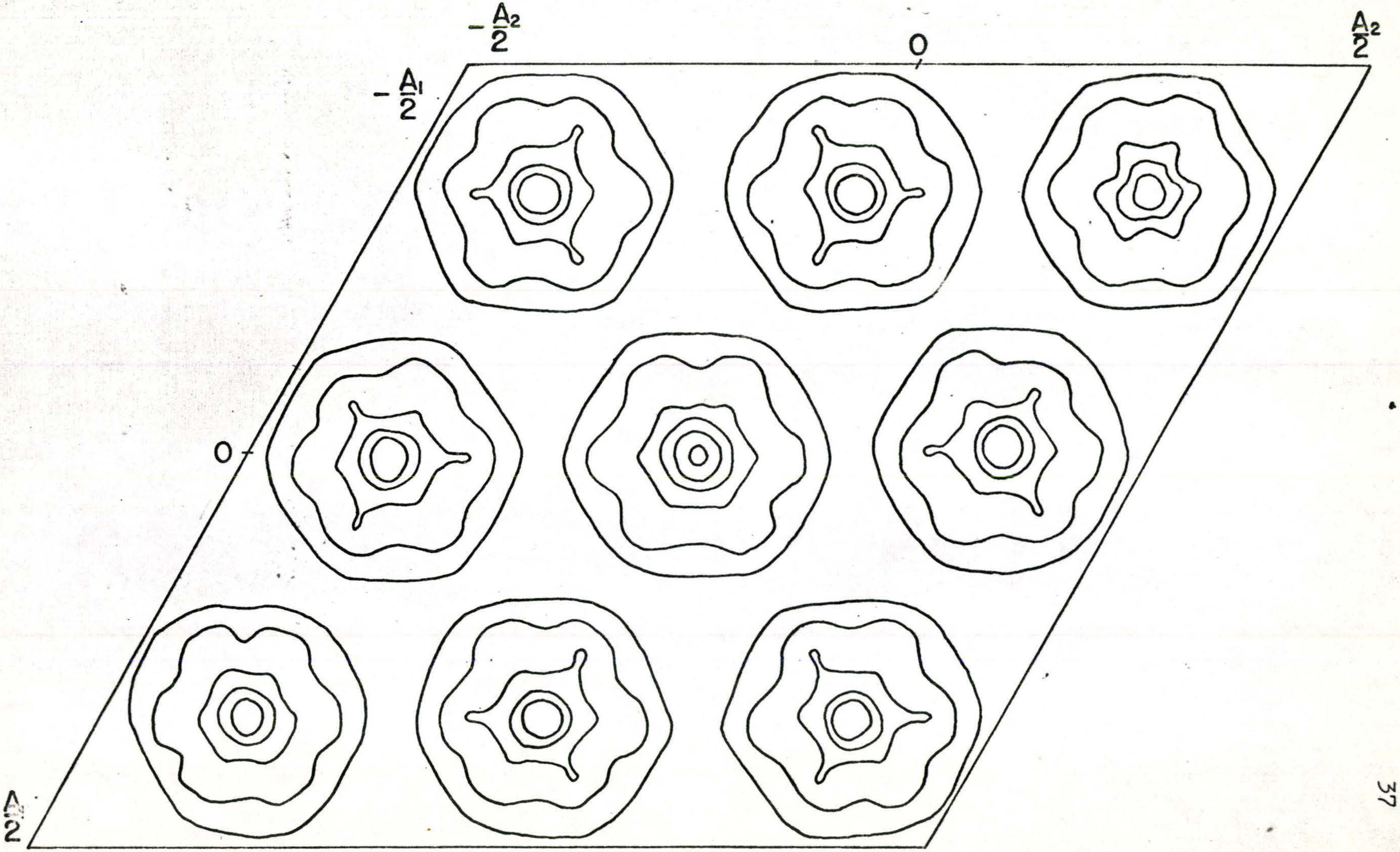
where δ is the root mean square displacement, d^* the magnitude of the reciprocal lattice vector $\underline{H}$. This is equivalent to the result above for the height of the origin peak. This analysis allowed Mackay to calculate the magnitude of the displacements involved in the structure of $Ca_3(PO_4)_2$, where M is 2.

The 'M=2' problem was carried further by Sakurai (1958), who introduced what he called the P_{odd} and P_{even} functions, which are the partial Patterson functions described above. The interpretation of these functions by Sakurai (1965) for the triclinic modification of quinhydrone ($C_6H_4(OH)_2, C_6H_4O_2$) is close to that above, although more qualitative.

The extension of the structure factor expressions and application of the subcell Patterson function to the 'M=3' case has been discussed by Stephens (1967).

The hk0 and hhℓ Patterson projections and the h0ℓ partial (h=0 mod 3 and h$\neq$0 mod 3) Patterson projections were constructed using the room temperature data. These calculations were performed, as were all subsequent Fourier series, using the FORTRAN language computer program MACFOU, written by the author. This program follows several of the suggestions of Rollett (1964) as to a versatile

Figure II-2.



The Patterson function of selenourea projected on (001).

basic Fourier program. These are the use of the Beevers and Lipson (1934) product form of the series and table look-up of trigonometric functions, variable grid sizes up to 1/120 of the unit cell edge, the possible choice of slant plane projections and sections, and applicability to all symmetries. This last requirement is satisfied by the generation of symmetry related reflections, together with their phase, according to the Waser (1955) formula,

$$F(R\underline{H})=e^{-2\pi i\underline{H}\cdot\underline{t}}F(\underline{H}) \qquad \text{(II-13)}$$

for a space group element consisting of a point operation R and a translational component $\underline{t}$.

The solution of the hk0 Patterson (Figure II-2) is particularly simple in retrospect, although initial attempts to conform to the model suggested by Kondrashev and Andreeva caused difficulties in determining the positions of the nine selenium atoms within the channels. In fact this projection contains nine almost identical regions, each the vector map of an equilateral triangle, with no other major features. This can be interpreted as nine such triangular groups of selenium atoms, equally spaced in this projection. For steric reasons each member of the group of three must be near to c/3 away from the others; this together with the pseudo-symmetry mentioned above yields approximate

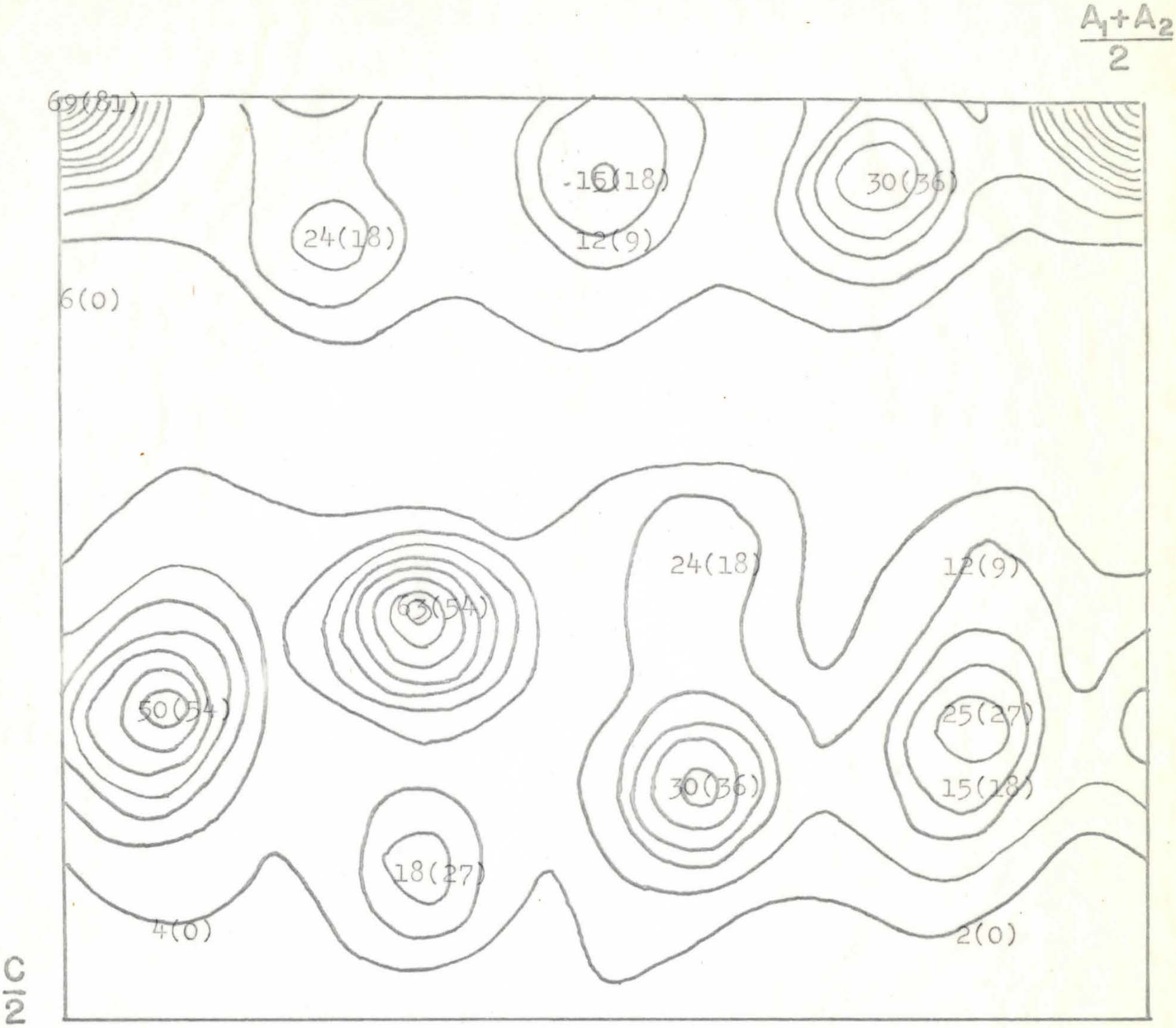


Figure II-3. The Patterson function of selenourea projected on ($\bar{1}10$). The number of Se-Se vectors contributing to each peak are illustrated. In parentheses are the corresponding values based on the assumed tripled structure.

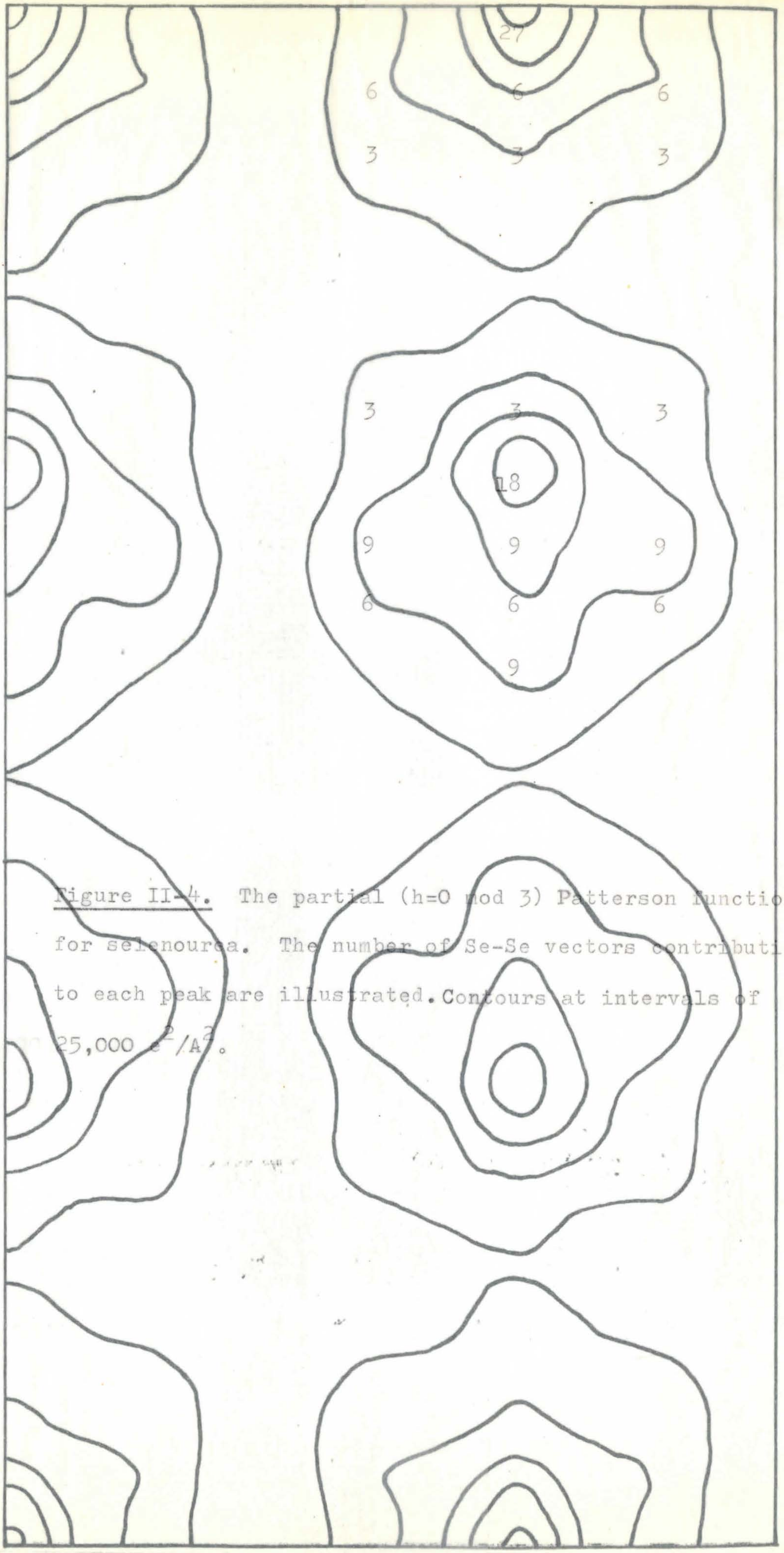


Figure II-4. The partial (h=0 mod 3) Patterson function for selenourea. The number of Se-Se vectors contributing to each peak are illustrated. Contours at intervals of $25,000\ e^2/A^2$.

positions for all selenium atoms. The deviations from this rhombohedral model of the structure were subsequently found to be nowhere greater than one Ångstrom, and their nature was a major problem in the structure determination.

The next stage was the solution, within the subcell, of the $hh\ell$ (equivalent to HOL, Figure II-3) and partial $h0\ell$ (h=0 mod 3, HHL, Figure II-4) Patterson projections. Compatible solutions for these were found assuming a near rhombohedral cell containing nine selenium atoms, and the origin for this structure was chosen so that the two-fold axis it contained passed through that origin. The structure then belonged to the space group $P3_112$ (full cell, $P3_121$ sub cell), and for some time refinement was carried out on this basis.

Structure factors were calculated for the room temperature data with -h+k=0 mod 3. The scattering factors used throughout were taken from International Tables for X-ray Crystallography, and were those of Freeman and Watson (1961) for selenium and Hoerni and Ibers (1951) for carbon and nitrogen. The calculated structure factors, $|F_c|e^{i\phi_c}$, used to compute the corresponding electron density and difference electron density

$$D(\underline{r}) = \sum_{\underline{H}} (|F_o| - |F_c|) e^{i(\phi_c - 2\pi \underline{H}.\underline{r})} \qquad \text{(II-14)}$$

syntheses. The carbon and nitrogen atoms were assigned positions based on peaks found on these maps. Least squares refinement of the positional parameters of this model, using the program MACLS written by J.S.Stephens, gave an unweighted R factor of about 0.2. The structure deduced at this stage contained spiral chains of selenourea molecules similar to those in the urea and thiourea hydrocarbon adducts.

The displacements giving rise to the true structure were determined in the following manner. The partial $h0\ell$ Patterson ($h \neq 0$ mod 3, Figure II-5) was examined and the prominent pattern of peaks on it were interpreted as arising from chains displaced as units (the within chain vectors are positive peaks) from their average positions, and in opposite directions to their subcell related chains (since the vectors between such chains correspond to minima). One subcell chain type only can be involved, since vectors between different chain types do not fall on features of this map. The vectors involved are illustrated in Figure II-5.

The particular chain involved and the extent of its displacement was found by scrutiny of the xxz electron density projection at this stage. The magnitudes of the electron density for the three independent selenium atoms on this map were 116, 100 and 100 electrons per square Ångstrom, where the latter two were related by the assumed 2-fold axis. A further pair of unexplained peaks of magnitude 19 $e/\text{Å}^2$ were found at a distance of 1.8Å from the 100 $e/\text{Å}^2$ peaks. When one chain was displaced the indicated

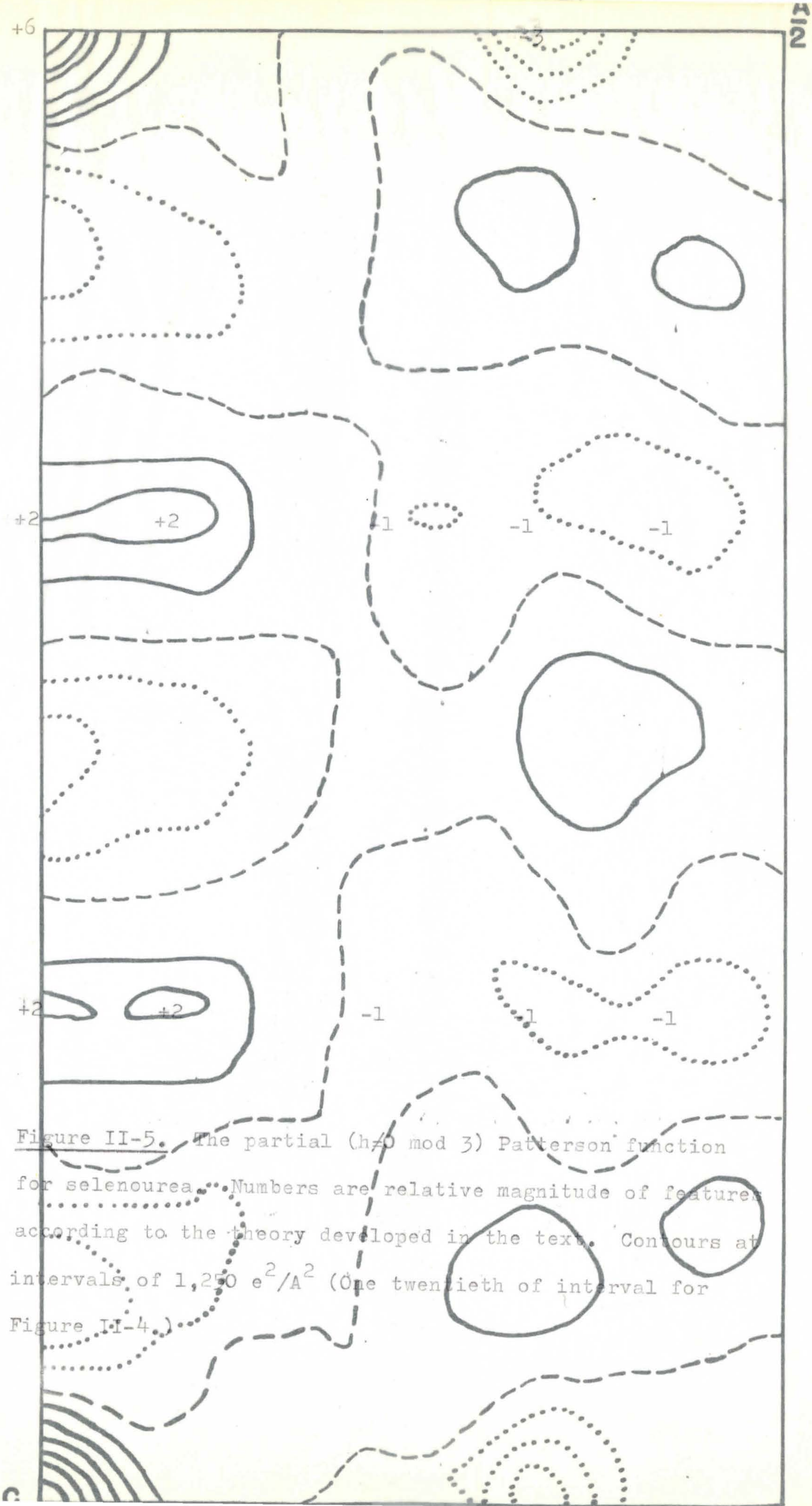


Figure II-5. The partial ($h \neq 0$ mod 3) Patterson function for selenourea. Numbers are relative magnitude of features according to the theory developed in the text. Contours at intervals of 1,250 e^2/A^2 (One twentieth of interval for Figure II-4.)

distance (the choice was dictated by the indexing of the other projections) the R factor of the $hh\ell$ projection was immediately reduced from 0.22 to 0.18.

Figure II-6 shows the relationship between the assumed $P3_112$ structure and the true structure. The small cell on the lower left illustrates the symmetry elements of the space group $P3_121$, that on the upper right the one three-fold axis of the three retained in the true structure, which is not the one at the small cell origin. The choice of large cell therefore requires the change of origin illustrated in the figure, to (2/3,1/3) in the small cell co-ordinates. The choice of the symmetry related point (1/3,2/3) as origin leads to the twin structure mentioned above.

Refinement.

The model described in the previous section was refined by least squares, using all the room temperature data and an overall temperature factor, to R=0.12. The data was then merged, that is, structure factors common to different layers were averaged, to form a set of only independent structure factors, using the layer scale constants determined by least squares. The individual measurements were weighted in these averages according to their previously assigned standard deviations, and the average values ascribed standard deviations accordingly. Even at this advanced stage of

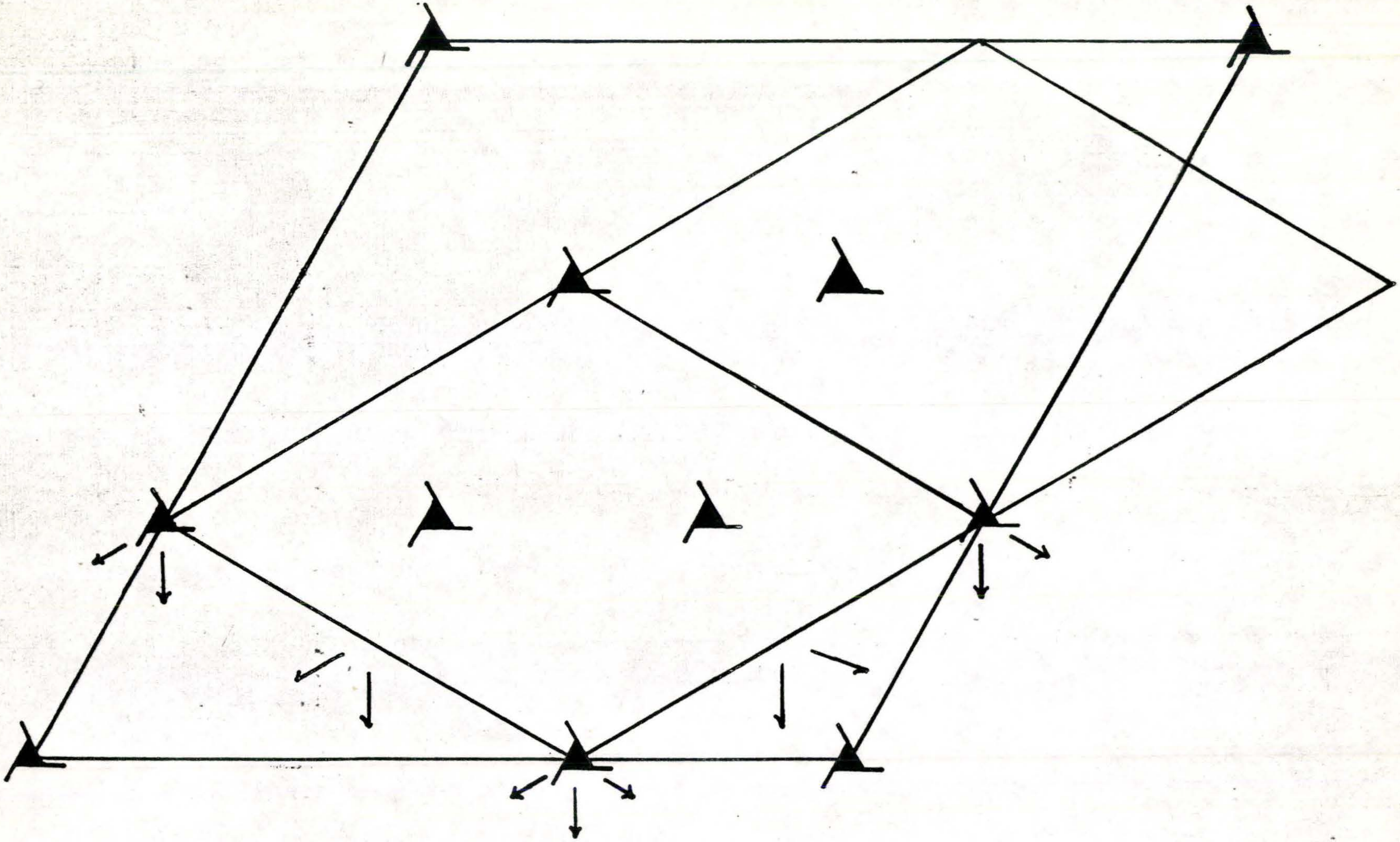


Figure II-6.

Relationship in position and symmetry between true unit cell and pseudosymmetric subcell.

refinement, the standard deviations in light atom co-ordinates were still about 0.1Å, and there appeared little hope of gaining worthwhile chemical information.

Some likely reasons for these difficulties have been discussed by Scheringer (1965). Three of the reasons he suggests for ill-conditioned least squares problems are applicable here. Foremost of course, is the smallness of the data set, consisting of 781 reflections, corresponding to projection data only. However, many crystal structures have been solved adequately with only projection data, which suggests other factors are operative. The possibility is always open to us to extend the data set, and this is exactly what we chose to do in the case of the low temperature work.

Unfortunately the other two effects are intrinsic to the selenourea structure analysis. One is the presence of atoms of widely differing scattering power; this is a more serious problem, and in earlier times would have been considered unsurmountable. But yet a third difficulty exists, that is, high correlations between parameters related by the elements of pseudo-symmetry outlined above. In this respect the structure of selenourea is very similar to that of guanidinium aluminum sulphate hexahydrate ($C(NH_2)_3Al(SO_4)_2 \cdot 6H_2O$, commonly called GASH) which was chosen by Scheringer as an example of this effect. GASH, a ferroelectric crystal, belongs to the polar trigonal space group P31m, with cell constants $a = 11.75$Å, $c = 8.94$Å (Geller and Booth, 1959). This cell contains three formula units, and is almost triply primitive, the subcell to supercell transformation being the same as for selenourea. The difficulties encountered in the refinement were discussed in detail by Geller and Katz (1962), and only prolonged least squares reiteration, using only fractional parameter changes, gave a satisfactory structure (Lingafelter, Orioli, Schein and Stewart, 1966). A similar cautious empirical approach has been followed in the case of selenourea.

In the light of these circumstances, it was clearly advantageous to divert attention to the low temperature data. This in turn was refined by least squares, using the room temperature co-ordinates as a starting point, and individual layer scale constants. The final individual layer R factors are listed in Table II-2. The data was then merged as described for the room temperature data, but now reflections occured up to five times, for, in hexagonal axes, such a set as the following are equivalent.

102	$h0\ell$
102	$hk2$
$01\bar{2}$	$h,h+1,\ell$
$01\bar{2}$	$h1\ell$
$\bar{1}12$	$h,h+2,\ell$

The selenium scattering curve was now corrected for the real part of the anomalous scattering for CuKα radiation. Although no attempt was made to discriminate between $hk\ell$ and $\overline{hk\ell}$ reflections in the data collection, the methods used ensured a similar number of each type, and therefore a systematic error in selenium z co-ordinate appreciably less than the possible value of 0.02Å suggested by Cruickshank and McDonald (1967). The final cycles were carried out using anisotropic temperature factors on the selenium atoms, and with the carbon parameters fixed. This was dòne because high correlations with other parameters caused large shifts to be calculated for several of these atoms, which would have produced chemically unlikely atomic configurations. The detailed carbon positions were chosen on the basis of chemical considerations, although their approximate positions can be derived from electron density maps. This process was continued until a minimum weighted R factor of 0.146 was obtained. The corresponding atomic parameters (with errors derived from least squares) and structure factors are listed in Table II-3 and Table II-4 respectively.

Although the majority of the room temperature light atom co-ordinates were identical, within the errors, to their low temperature equivalents, several had to be adjusted in the light of the low temperature refinement. This was dòne, the light atom positions were fixed, and a subsequent two further cycles of refinement brought the weighted R factor for this data to 0.116. The final parameters can be found in TableII-5 and the corresponding structure factors in Table II-6.

The final co-ordinates mentioned above were used to compute interatomic distances and angles, using the program ERROR written

TABLE II-3.

Final atomic parameters at -100°C.

Atom	Number	x	y	z	B
Se	1	0.9318(5)	0.9654(5)	0.4280	
	2	0.6054(5)	0.2893(6)	0.5708(6)	
	3	0.2625(6)	0.6397(6)	0.5537(6)	
	6	0.6041(6)	0.6325(6)	0.8598(7)	
	4	0.2898(6)	0.9740(6)	0.8646(7)	
	5	0.9351(6)	0.3060(6)	0.8564(7)	
	8	0.9417(7)	0.6444(6)	0.1384(8)	
	9	0.6132(6)	0.9727(6)	0.1512(7)	
	7	0.2622(6)	0.3000(6)	0.1489(7)	
C	1	0.072(6)	0.038(6)	0.426(6)	2.0
	2	0.742(6)	0.387(6)	0.577(6)	2.0
	3	0.402(6)	0.671(6)	0.540(6)	2.0
	4	0.428(6)	0.056(6)	0.855(6)	2.0
	5	0.076(6)	0.346(6)	0.852(6)	2.0
	6	0.730(6)	0.645(6)	0.851(6)	2.0
	7	0.389(6)	0.414(6)	0.152(6)	2.0
	8	0.083(6)	0.727(6)	0.148(6)	2.0
	9	0.752(6)	0.036(6)	0.144(6)	2.0
N1	1	0.112(5)	0.079(5)	0.335(4)	3.3(14)
	2	0.795(4)	0.425(4)	0.488(4)	1.6(11)
	3	0.454(4)	0.705(4)	0.443(4)	1.9(11)
	4	0.480(3)	0.103(3)	0.769(3)	0.0(7)
	5	0.123(5)	0.363(5)	0.753(4)	3.4(14)
	6	0.782(4)	0.676(4)	0.762(4)	1.8(11)
	7	0.437(3)	0.480(3)	0.075(3)	0.2(8)
	8	0.134(4)	0.793(4)	0.068(3)	0.9(9)
	9	0.806(3)	0.089(3)	0.060(3)	0.5(8)
N2	1	0.122(4)	0.041(4)	0.512(3)	0.9(9)
	2	0.810(5)	0.416(5)	0.656(4)	4.1(15)
	3	0.437(3)	0.654(3)	0.631(3)	0.6(8)
	4	0.478(5)	0.063(5)	0.947(4)	4.7(16)
	5	0.126(4)	0.357(4)	0.941(4)	2.0(11)
	6	0.779(4)	0.630(4)	0.923(3)	1.6(11)
	7	0.446(4)	0.442(4)	0.239(3)	1.1(10)
	8	0.132(4)	0.720(4)	0.233(4)	2.5(12)
	9	0.799(4)	0.032(4)	0.231(3)	1.9(11)

(Continued overleaf)

TABLE II-3

Final atomic parameters at -100°C.

(continued)

Anisotropic temperature factor components (X 10^4).

Atom	Number	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Se	1	14(4)	26(4)	8(4)	13(4)	2(3)	-3(4)
	2	22(5)	14(5)	29(4)	0(5)	-12(4)	-10(4)
	3	17(5)	40(5)	35(4)	14(5)	-6(5)	-17(5)
	4	13(4)	23(4)	29(4)	13(4)	5(4)	9(4)
	5	4(5)	20(5)	29(5)	4(5)	-9(5)	-10(5)
	6	11(5)	29(5)	42(4)	11(5)	10(5)	-1(5)
	7	15(4)	40(4)	43(4)	11(4)	-3(4)	-5(4)
	8	18(6)	27(5)	17(6)	6(5)	-3(6)	1(5)
	9	9(5)	20(5)	17(4)	6(5)	1(5)	1(4)

TABLE II-4.

H	L	F0	FC	PHI
K= 0				
0	3	506	647	189
0	6	98	86	60
0	9	51	61	309
0	12	79	49	302
0	15•	45	65	91
1	-16•	23	40	19
1	-15•	27	14	352
1	-14•	30	8	51
1	-13	32	23	145
1	-12	107	106	289
1	-11	28	27	290
1	-10	35	27	308
1	-9	98	85	129
1	-8	21	12	159
1	-7	41	33	136
1	-6	91	80	81
1	-5	53	45	174
1	-4	46	38	331
1	-3	215	210	279
1	-2•	9	7	335
1	-1	20	20	145
1	1•	6	7	339
1	2	9	12	57
1	3	182	164	90
1	4	33	28	142
1	5	19	27	248
1	6	59	57	228
1	7	28	23	245
1	8	38	32	12
1	9	78	63	312
1	10	28	31	44
1	11	47	40	104
1	12	50	40	21
1	13•	32	15	255
1	14	34	38	249
1	15	46	55	150
1	16•	23	22	182
2	-16•	23	32	274
2	-15•	26	28	221
2	-14•	30	12	39
2	-13	32	40	73
2	-12	55	28	304
2	-11	39	28	262
2	-10	25	24	244
2	-9	63	61	53
2	-8	55	49	63
2	-7•	20	11	99
2	-6	43	39	130
2	-5	77	69	205
2	-4	79	77	10
2	-3	103	107	271
2	-2	32	35	342
2	-1	19	16	190
2	0•	14	8	49
2	1	31	28	326
2	2	34	36	202
2	3	151	150	80
2	4	99	84	141
2	5	119	110	4
2	6	80	66	282
2	7	29	32	260
2	8	46	39	254
2	9	108	102	246
2	10	32	29	5
2	11	47	37	115
2	12	115	120	62
2	13•	32	32	174
2	14•	30	5	265
2	15•	26	20	191
2	16•	23	20	45
3	-16•	83	18	3
3	-15•	78	41	293
3	-14	141	98	242
3	-13•	88	45	196
3	-12•	73	22	120
3	-11	125	89	48
3	-10	131	122	59
3	-9•	65	35	31
3	-8•	60	33	160
3	-7	235	263	260
3	-6	116	111	327
3	-5•	46	25	326
3	-4	235	211	76
3	-3	373	399	173
3	-2	77	81	222
3	-1	34	20	40
3	0	597	582	358
3	1	46	33	18
3	2	76	65	261
3	3	386	397	193
3	4	276	224	67
3	5	75	57	187
3	6	144	104	41
3	7	334	260	259
3	8•	60	50	327
3	9•	65	36	320
3	10	137	99	82
3	11	125	84	67
3	12•	73	18	254
3	13•	88	20	306
3	14	116	89	253
3	15•	78	44	85
3	16•	83	21	165
4	-16•	84	29	28
4	-15•	77	24	313
4	-14•	82	24	87
4	-13•	87	35	303
4	-12•	90	9	34
4	-11	84	63	336
4	-10•	71	42	149
4	-9•	67	15	241
4	-8•	62	43	221
4	-7•	58	9	266
4	-6	75	70	112
4	-5	88	80	146
4	-4	103	104	336
4	-3	86	92	294
4	-2	57	38	1
4	-1	146	146	143
4	0	55	39	195
4	1	128	117	336
4	2•	39	30	63
4	3	69	63	97
4	4	84	76	157
4	5	92	72	283
4	6	64	36	222
4	7	58	47	191
4	8	68	67	31
4	9•	67	20	347
4	10•	71	66	351
4	11•	73	45	125
4	12•	90	12	26
4	13•	87	17	38
4	14•	82	52	250
4	15•	77	37	149
4	16•	84	40	136
5	-15•	78	30	302
5	-14•	80	27	328
5	-13•	86	64	63
5	-12•	90	21	83
5	-11•	73	19	273
5	-10•	72	9	277
5	-9•	69	19	153
5	-8•	65	42	71
5	-7	60	56	222
5	-6•	57	33	268
5	-5	74	66	170
5	-4	69	73	11
5	-3•	39	38	29
5	-2	127	145	321
5	-1	54	55	273
5	0	37	35	54
5	1•	42	34	262
5	2	122	113	156
5	3	39	45	227
5	4	107	106	129
5	5	111	90	344
5	6	57	27	308
5	7	60	26	340
5	8•	65	25	210
5	9•	69	15	313
5	10•	72	43	288
5	11•	73	41	97
5	12•	90	12	44
5	13•	86	14	130
5	14•	80	8	198
5	15•	78	30	175
6	-15•	80	41	1
6	-14	164	134	229
6	-13•	83	54	220
6	-12•	88	28	187
6	-11	119	108	45
6	-10	166	183	58
6	-9•	71	17	118
6	-8•	68	19	183
6	-7	189	259	229
6	-6	60	29	15
6	-5•	57	11	339
6	-4	151	204	50
6	-3	121	112	258
6	-2	58	47	193
6	-1	73	64	273
6	0	134	128	103
6	1	58	46	247
6	2•	49	34	266
6	3	126	121	276
6	4	191	211	39
6	5	65	66	118
6	6•	60	39	103
6	7	279	247	233
6	8	68	67	287
6	9•	71	4	320
6	10	166	153	71
6	11	137	102	79
6	12•	88	8	131
6	13•	83	48	285
6	14	125	125	245
6	15•	80	10	194
7	-14•	77	8	44
7	-13•	81	56	302
7	-12•	86	63	60
7	-11•	90	48	356
7	-10•	73	70	128
7	-9•	73	54	247
7	-8•	70	21	153
7	-7•	67	13	198
7	-6•	64	64	205
7	-5•	60	28	142
7	-4	85	121	303
7	-3	105	111	29
7	-2•	54	22	229
7	-1	123	125	134
7	0	49	47	180
7	1	92	88	340
7	2	75	77	25
7	3	65	73	219
7	4	58	29	157
7	5•	60	50	238
7	6•	64	43	15
7	7•	67	65	159
7	8•	70	43	342
7	9•	73	35	28
7	10•	73	55	335
7	11•	90	29	138
7	12•	86	37	155
7	13•	81	32	68
7	14•	77	13	265
8	-14•	82	18	326
8	-13•	80	29	75
8	-12•	83	37	58
8	-11•	88	18	325
8	-10•	90	33	1
8	-9•	73	67	192
8	-8•	73	21	180
8	-7•	70	79	226
8	-6•	67	58	312
8	-5	65	79	106
8	-4	62	70	72
8	-3	60	48	31
8	-2	102	114	310
8	-1	74	58	289
8	0	48	29	72
8	1•	58	28	175
8	2	68	45	147
8	3	103	110	222
8	4	62	68	114
8	5	78	81	286
8	6•	67	16	145
8	7•	70	65	342
8	8•	73	45	176
8	9	73	81	17
8	10•	90	40	224
8	11•	88	6	354
8	12•	83	57	203
8	13•	80	4	342
8	14•	62	10	163
9	-13•	80	21	231
9	-12•	80	19	190
9	-11•	85	55	37
9	-10	101	57	33
9	-9•	90	31	149
9	-8•	73	17	220
9	-7	97	122	218
9	-6•	71	60	93
9	-5•	69	12	221
9	-4	98	108	55
9	-3	227	249	295
9	-2•	64	28	3
9	-1	63	64	250
9	0	409	390	117
9	1	63	53	183
9	2•	64	5	117
9	3	244	265	308
9	4	93	119	33
9	5•	69	40	92
9	6•	71	68	162
9	7	125	138	226
9	8•	73	48	267
9	9•	90	19	74
9	10	123	68	54
9	11•	85	44	58
9	12•	80	17	60
9	13•	80	26	305
10	-13•	86	47	287
10	-12•	78	40	68
10	-11•	81	18	193
10	-10•	85	33	99
10	-9•	88	29	238
10	-8•	90	20	339
10	-7•	73	2	151
10	-6•	73	80	225
10	-5•	72	39	279
10	-4•	71	45	284
10	-3	110	114	33
10	-2•	69	52	112
10	-1•	68	33	152
10	0	38	34	121
10	1•	68	9	52
10	2•	69	29	341
10	3	84	85	217
10	4•	71	54	268
10	5•	72	12	179
10	6•	73	67	29
10	7•	73	33	131
10	8•	90	11	262
10	9•	88	23	319
10	10•	85	21	311
10	11•	81	31	176
10	12•	78	43	120
10	13•	86	36	64
11	-12•	89	43	22
11	-11•	79	34	343
11	-10•	82	40	24
11	-9•	85	77	184
11	-8•	88	55	185
11	-7•	90	39	260
11	-6•	91	54	337
11	-5•	73	26	14
11	-4	73	74	109
11	-3•	64	16	27
11	-2•	73	25	265
11	-1•	73	19	267
11	0•	40	25	118
11	1•	73	10	94
11	2•	73	61	306
11	3	64	45	224
11	4•	73	35	196
11	5•	73	32	146
11	6•	91	16	96
11	7•	90	36	5
11	8•	88	43	94
11	9•	85	80	14
11	10•	82	24	167
11	11•	79	45	288
11	12$	164	94	200
12	-11•	90	17	154
12	-10•	79	48	219
12	-9•	81	22	201
12	-8•	84	18	244
12	-7	67	74	37
12	-6	89	64	78
12	-5•	91	18	89
12	-4•	91	43	182
12	-3	188	185	291
12	-2•	74	47	346
12	-1•	76	37	255
12	0	258	290	121
12	1•	76	46	180
12	2•	74	31	59
12	3	185	219	308
12	4•	91	19	227
12	5•	91	21	4
12	6	69	68	147
12	7	87	42	7
12	8•	84	12	159
12	9•	81	30	61
12	10•	79	21	196
12	11•	90	18	250
13	-10•	89	22	227
13	-9•	82	37	8
13	-8•	80	28	331
13	-7•	83	37	359
13	-6•	65	63	208
13	-5•	87	46	251
13	-4•	89	46	129
13	-3•	77	55	48
13	-2•	91	32	59
13	-1•	93	39	272
13	0•	49	11	282
13	1•	93	51	127
13	2•	91	30	167
13	3•	77	76	222
13	4•	89	42	269
13	5•	87	62	14
13	6•	85	65	30
13	7•	83	24	11
13	8•	80	34	180
13	9•	82	21	176
13	10•	89	20	173
14	-8•	86	45	167
14	-7•	80	44	301
14	-6•	81	42	11
14	-5•	63	66	302
14	-4•	84	48	151
14	-3•	86	6	259
14	-2	88	66	95
14	-1•	90	47	64
14	0•	46	20	146
14	1•	90	22	331
14	2	122	100	283
14	3•	86	25	331
14	4•	84	63	235
14	5•	83	83	128
14	6•	81	14	182
14	7•	80	34	71
14	8•	86	23	33
15	-7$	164	103	17
15	-6•	87	25	91
15	-5•	84	5	42
15	-4•	82	59	184
15	-3	102	51	297
15	-2•	83	28	349
15	-1•	81	7	336
15	0	78	85	133
15	1•	81	18	136
15	2•	63	21	17
15	3	115	90	319
15	4•	82	53	189
15	5•	84	23	250
15	6•	87	46	149
15	7$	204	83	5
16	-3•	90	35	102
16	-2•	77	38	334
16	-1	86	78	296
16	0•	32	31	294
16	1•	65	67	136
16	2•	77	62	131
16	3•	90	27	192
K= 1				
1	-16•	40	32	334
1	-15	209	176	174
1	-14•	50	16	357
1	-13•	48	20	113
1	-12	230	221	349
1	-11•	39	11	237
1	-10•	37	13	37
1	-9	107	108	148
1	-8	140	126	118
1	-7	30	20	326
1	-6	48	58	279
1	-5	218	197	306
1	-4	177	173	226
1	-3	81	74	112
1	-2	40	38	139
1	-1	170	192	60
1	0•	13	10	159
1	1•	15	8	301
1	2	113	127	253
1	3	311	331	352
1	4	38	33	36
1	5	104	97	80
1	6	395	430	180
1	7	37	40	237
1	8	36	12	21
1	9	328	382	4
1	10•	37	9	337
1	11•	39	32	273
1	12	162	146	200
1	13•	48	28	132
1	14•	50	17	132
1	15•	44	34	94
1	16	52	47	308
2	-15•	29	5	210
2	-14	32	33	200
2	-13	44	52	18
2	-12	104	101	307
2	-11	63	69	8
2	-10	87	81	174
2	-9	99	83	127
2	-8	55	47	207
2	-7	27	22	30
2	-6	62	55	102
2	-5	98	83	207
2	-4	129	118	334
2	-3	115	107	268
2	-2	54	50	346
2	-1	59	52	153
2	0	72	67	316
2	1•	15	10	269
2	2	58	49	163
2	3	123	125	106
2	4	82	82	165
2	5	56	58	330
2	6	50	38	253
2	7	48	38	315
2	8•	24	22	164
2	9	41	33	294
2	10•	27	11	327
2	11	43	36	70
2	12	49	44	35
2	13	39	17	68
2	14•	32	35	221
2	15•	29	48	161
3	-15•	25	54	211
3	-14•	29	29	301
3	-13•	31	23	14
3	-12	44	44	343
3	-11•	26	22	353
3	-10	48	48	116
3	-9	38	35	95
3	-8	49	39	139
3	-7	50	53	236
3	-6	59	44	97
3	-5•	17	9	23
3	-4	92	85	0
3	-3	94	94	276
3	-2	63	55	267
3	-1	80	75	21
3	0	41	33	306
3	1•	13	32	244
3	2	127	122	168
3	3	99	101	97
3	4	87	84	153
3	5	64	55	334
3	6	94	88	304
3	7	36	44	4
3	8	58	58	315
3	9	53	40	192
3	10	44	37	278
3	11	75	82	142
3	12•	33	19	30
3	13	48	48	104
3	14•	29	36	11
3	15•	25	21	56
4	-14•	142	23	341
4	-13•	151	29	123
4	-12•	158	59	348
4	-11•	128	93	207
4	-10•	126	24	106
4	-9•	120	55	165
4	-8	184	177	56
4	-7•	104	32	354
4	-6	97	52	312
4	-5	218	195	261
4	-4	225	230	228
4	-3•	37	23	213
4	-2	127	111	87
4	-1	457	575	54
4	0	66	57	171
4	1•	46	13	146
4	2	384	464	247
4	3	138	129	15
4	4•	83	33	305
4	5	140	122	85
4	6	237	229	205
4	7•	104	29	211
4	8•	112	55	24
4	9	153	143	23
4	10•	126	49	273
4	11•	128	33	268
4	12•	158	42	238
4	13•	151	92	73
4	14•	142	50	155
5	-14•	138	55	202
5	-13•	148	30	22
5	-12•	156	35	327
5	-11•	129	86	359
5	-10•	128	71	186
5	-9•	123	33	199
5	-8•	117	19	214
5	-7•	109	50	101
5	-6•	103	17	180
5	-5	107	68	151
5	-4	141	150	313
5	-3	41	42	41
5	-2	63	39	282
5	-1	87	69	140
5	0	55	51	250
5	1•	51	30	46
5	2	85	70	145
5	3	56	62	162
5	4•	90	10	88
5	5	96	85	335
5	6•	103	39	337
5	7•	109	35	176
5	8•	117	37	173
5	9•	123	25	163
5	10•	128	25	14
5	11•	129	52	41
5	12•	156	14	13
5	13•	148	27	348
5	14•	138	61	221
6	-13•	143	39	341
6	-12•	153	23	28
6	-11•	158	51	297
6	-10•	128	62	118
6	-9•	127	48	132
6	-8•	121	43	121
6	-7•	115	68	258
6	-6•	108	63	250
6	-5	104	77	78
6	-4•	98	27	321
6	-3	87	64	23
6	-2•	70	42	305
6	-1•	57	44	352
6	0•	28	16	253
6	1	90	100	277
6	2	111	105	162
6	3	48	45	173
6	4	119	124	97
6	5•	104	40	337
6	6•	108	80	328
6	7•	115	68	307
6	8•	121	61	300
6	9•	127	29	121
6	10•	128	42	260
6	11•	158	100	137
6	12•	153	41	218
6	13•	143	45	114
7	-13•	139	22	184
7	-12•	148	82	107
7	-11•	156	78	187
7	-10•	129	26	109
7	-9•	128	56	235
7	-8	161	163	19
7	-7•	121	41	10
7	-6•	115	50	15
7	-5	172	196	210
7	-4	164	182	227
7	-3	51	36	254
7	-2	95	82	67
7	-1	312	338	58
7	0	53	51	161
7	1•	63	29	348
7	2	284	337	242
7	3	130	104	104
7	4•	105	17	261
7	5	134	134	74
7	6	172	223	301
7	7•	121	45	81

• UNOBSERVED REFLECTION. F0 IS MINIMUM OBSERVABLE
$ ABSORPTION CORRECTION UNRELIABLE

Observed and calculated structure factors at -100°C.

TABLE II-4 (continued)

H	L	FO	FC	PHI
7	8•	126	44	343
7	9	156	170	122
7	10•	129	59	240
7	11•	156	30	221
7	12•	148	52	300
7	13•	139	61	42
8	-12•	143	63	42
8	-11•	151	16	54
8	-10•	157	27	278
8	-9•	129	63	220
8	-8•	128	44	311
8	-7•	126	73	115
8	-6•	122	37	199
8	-5•	118	37	108
8	-4•	113	96	308
8	-3	64	67	25
8	-2•	85	49	223
8	-1•	69	54	179
8	0	41	39	54
8	1•	69	38	74
8	2•	85	49	142
8	3	74	75	215
8	4•	113	59	314
8	5•	118	85	325
8	6•	122	55	341
8	7•	126	79	149
8	8•	128	43	150
8	9•	129	50	105
8	10•	157	16	349
8	11•	151	26	40
8	12•	143	16	264
9	-13•	144	15	210
9	-12•	140	21	83
9	-11•	145	39	283
9	-10•	152	28	89
9	-9•	158	27	131
9	-8•	129	24	188
9	-7•	128	61	286
9	-6•	127	80	235
9	-5•	124	54	65
9	-4•	121	51	144
9	-3	127	134	23
9	-2•	92	43	336
9	-1•	75	35	29
9	0	60	75	208
9	1	75	83	217
9	2•	92	21	268
9	3	76	74	192
9	4•	121	76	89
9	5•	124	6	151
9	6•	127	58	14
9	7•	128	55	299
9	8•	129	16	276
9	9•	158	30	42
9	10•	152	2	159
9	11•	145	10	119
9	12•	140	47	190
10	-11•	138	64	143
10	-10•	146	8	125
10	-9•	152	61	258
10	-8•	157	61	331
10	-7•	129	19	85
10	-6•	129	23	31
10	-5•	128	37	177
10	-4•	128	42	282
10	-3•	63	27	292
10	-2•	97	23	41
10	-1•	79	37	105
10	0•	39	10	100
10	1•	79	12	295
10	2•	97	54	253
10	3	150	152	117
10	4•	128	37	178
10	5•	128	72	84
10	6	212	251	300
10	7•	129	55	7
10	8•	157	32	298
10	9	214	195	125
10	10•	146	46	183
10	11•	138	25	232
11	-10•	138	48	286
11	-9•	146	57	222
11	-8•	151	23	308
11	-7•	156	17	102
11	-6•	159	10	5
11	-5•	130	25	321
11	-4•	129	40	23
11	-3•	64	21	308
11	-2•	100	54	200
11	-1•	82	65	219
11	0	66	70	76
11	1•	82	73	60
11	2•	100	22	83
11	3	78	79	230
11	4•	129	53	280
11	5•	130	15	300
11	6•	159	24	328
11	7•	156	18	102
11	8•	151	13	178
11	9•	146	56	71
11	10•	138	12	184
12	-9•	141	8	2
12	-8•	144	49	249
12	-7•	149	30	352
12	-6•	153	64	162
12	-5•	157	32	110
12	-4•	159	56	140
12	-3	114	108	2
12	-2•	123	40	1
12	-1•	101	19	57
12	0	73	75	205
12	1•	101	35	170
12	2•	123	67	300
12	3•	78	30	141
12	4•	159	47	288
12	5•	157	32	156
12	6•	153	47	5
12	7•	149	26	157
12	8•	144	51	96
12	9•	141	13	277
13	-7•	141	19	126
13	-6•	146	15	145
13	-5•	149	57	33
13	-4•	152	94	10
13	-3•	74	20	98
13	-2•	117	29	274
13	-1	156	159	188
13	0	48	34	272
13	1•	97	9	171
13	2	149	117	9
13	3	94	92	104
13	4•	152	46	159
13	5•	149	33	187
13	6•	146	143	298
13	7•	141	57	333
14	-5•	140	38	327
14	-4•	144	54	76
14	-3•	147	38	200
14	-2•	105	51	171
14	-1•	87	65	214
14	0	43	34	47
14	1•	87	22	38
14	2•	105	45	346
14	3•	147	38	243
14	4•	144	26	239
14	5•	140	50	111
15	-2•	88	32	341
15	-1•	73	27	160
15	0	38	48	190
15	1•	73	51	62
15	2•	88	37	334
16	-2•	61	30	207
16	-1	104	128	184
16	0•	26	38	255
16	1•	53	23	113
16	2	82	126	6
K= 2				
1	-15•	29	17	220
1	-14•	32	30	261
1	-13•	35	28	12
1	-12	42	27	242
1	-11	33	35	47
1	-10	39	54	142
1	-9	66	68	44
1	-8	59	50	180
1	-7	28	21	192
1	-6	44	34	142
1	-5	46	46	281
1	-4	139	108	330
1	-3	110	93	284
1	-2	46	39	107
1	-1	46	43	120
1	0	72	55	240
1	1•	15	13	129
1	2	64	60	135
1	3	162	169	77
1	4	79	82	230
1	5	116	118	309
1	6	109	97	255
1	7	50	37	52
1	8•	24	11	63
1	9	76	66	246
1	10	33	40	109
1	11	61	66	148
1	12	97	101	79
1	13•	35	43	284
1	14•	32	21	294
1	15	38	21	314
2	-15•	43	35	283
2	-14•	48	16	80
2	-13	186	143	50
2	-12	101	69	146
2	-11•	40	19	297
2	-10	100	86	216
2	-9	239	210	353
2	-8•	33	11	121
2	-7	60	54	323
2	-6	355	363	181
2	-5	90	72	99
2	-4	76	66	146
2	-3	214	223	2
2	-2	57	52	286
2	-1	22	19	297
2	0	59	44	353
2	1	31	22	265
2	2	149	148	49
2	3	27	28	202
2	4	132	130	322
2	5	257	277	238
2	6	32	39	110
2	7	41	41	172
2	8	283	322	63
2	9	102	85	207
2	10•	38	25	172
2	11	139	141	256
2	12	136	131	8
2	13•	52	24	6
2	14•	48	26	163
2	15	59	95	190
3	-15•	27	23	101
3	-14•	31	7	110
3	-13	80	68	352
3	-12•	36	30	309
3	-11•	29	19	275
3	-10	91	94	161
3	-9	33	15	184
3	-8	45	45	38
3	-7•	24	18	226
3	-6	35	28	100
3	-5	111	100	206
3	-4	102	96	327
3	-3	99	103	300
3	-2	38	45	44
3	-1	31	39	112
3	0	72	66	153
3	1	41	45	314
3	2	94	107	155
3	3	40	38	166
3	4	65	70	204
3	5	100	100	304
3	6	29	34	156
3	7•	24	9	54
3	8	52	50	53
3	9	56	51	314
3	10•	28	38	29
3	11	50	47	156
3	12•	36	30	105
3	13•	34	31	212
3	14•	31	20	265
3	15•	27	6	70
4	-15•	24	19	332
4	-14•	27	23	228
4	-13	59	52	48
4	-12	42	34	190
4	-11	33	29	352
4	-10	28	29	183
4	-9•	25	28	56
4	-8	36	30	154
4	-7	48	41	156
4	-6	21	17	238
4	-5	22	11	136
4	-4	110	110	321
4	-3	28	23	345
4	-2	46	48	329
4	-1	97	112	130
4	0	41	37	50
4	1•	16	11	122
4	2	56	58	150
4	3•	17	21	197
4	4	30	39	98
4	5	86	101	325
4	6	43	48	267
4	7	22	17	314
4	8	24	26	316
4	9	29	43	331
4	10	30	54	272
4	11	89	110	133
4	12	41	48	139
4	13•	30	22	113
4	14•	27	28	286
4	15•	24	34	294
5	-11•	49	3	54
5	-10	129	129	221
5	-9	73	59	100
5	-8•	37	16	91
5	-7	35	50	332
5	-6	132	117	270
5	-5	51	63	331
5	-4	48	42	129
5	-3	53	40	101
5	-2	133	158	203
5	-1	26	28	42
5	0	28	14	179
5	1	192	165	48
5	2	151	135	58
5	3•	28	19	102
5	4	71	66	239
5	5	294	344	237
5	6	42	45	280
5	7•	35	28	169
5	8	284	337	58
5	9•	39	10	170
5	10•	39	7	303
5	11	132	164	251
6	-11•	48	27	253
6	-10	94	98	174
6	-9	48	51	254
6	-8•	38	43	7
6	-7	37	36	354
6	-6	57	51	211
6	-5	54	44	174
6	-4•	32	27	342
6	-3	50	46	19
6	-2	29	25	86
6	-1•	29	25	69
6	0•	30	13	47
6	1	53	49	329
6	2	116	101	172
6	3	64	63	194
6	4	52	48	151
6	5	85	103	328
6	6•	35	31	333
6	7	42	55	204
6	8•	38	16	40
6	9•	40	22	53
6	10	40	65	60
6	11	68	54	139
7	-10•	49	25	268
7	-9•	40	27	201
7	-8•	40	2	180
7	-7	38	49	123
7	-6•	37	32	296
7	-5	67	70	102
7	-4	74	79	301
7	-3	33	34	75
7	-2	84	77	317
7	-1	56	42	121
7	0	33	27	22
7	1	48	40	235
7	2	41	30	229
7	3	122	138	214
7	4	48	67	75
7	5•	35	19	314
7	6	67	88	49
7	7•	38	16	56
7	8•	40	11	333
7	9	40	60	337
7	10	49	86	254
8	-9	187	184	111
8	-8•	40	7	138
8	-7	44	52	37
8	-6	247	236	309
8	-5	79	69	336
8	-4•	36	23	203
8	-3	163	141	144
8	-2	184	172	154
8	-1•	35	34	224
8	0•	36	14	141
8	1	149	146	337
8	2	99	86	56
8	3	48	23	19
8	4	66	70	177
8	5	152	164	246
8	6	47	43	271
8	7•	40	37	89
8	8	137	162	70
8	9•	49	32	352
9	-8•	49	30	50
9	-7	46	45	329
9	-6•	40	39	214
9	-5•	39	26	308
9	-4•	39	22	118
9	-3	92	92	63
9	-2	58	44	170
9	-1•	37	33	285
9	0	47	20	231
9	1•	37	28	305
9	2	56	53	156
9	3•	38	23	221
9	4	58	54	48
9	5	59	52	357
9	6•	40	50	302
9	7•	40	77	224
9	8•	49	55	209
10	-6•	49	12	307
10	-5	40	41	108
10	-4•	40	56	91
10	-3•	40	42	48
10	-2•	40	18	13
10	-1•	40	5	237
10	0	59	57	7
10	1	68	50	245
10	2	65	57	287
10	3	130	147	194
10	4•	40	21	74
10	5•	40	31	83
10	6•	49	95	21
11	-5	62	54	319
11	-4•	49	21	245
11	-3	161	152	123
11	-2	104	89	112
11	-1•	41	29	191
11	0	44	33	349
11	1	129	105	290
11	2	40	26	111
11	3•	40	26	286
11	4	67	57	127
11	5	102	91	355
12	-3•	76	60	26
12	-2	76	48	154
12	-1•	50	27	248
12	0	54	48	195
12	1	61	30	142
12	2	49	22	267
12	3•	76	26	21
13	-2•	111	60	76
13	-1•	92	64	249
13	0•	45	18	322
13	1•	92	36	288
13	2•	111	24	296
14	-2•	96	45	2
14	-1•	80	16	120
14	0	41	33	342
14	1	80	65	190
14	2•	96	50	206
15	-2•	75	16	241
15	-1•	63	31	166
15	0•	31	41	169
15	1•	63	49	117
15	2•	75	36	282
K= 3				
1	-15	38	24	25
1	-14•	29	16	345
1	-13	46	43	343
1	-12	58	53	251
1	-11	43	35	101
1	-10	83	59	174
1	-9	34	20	79
1	-8	53	47	297
1	-7	44	41	109
1	-6	98	94	99
1	-5	60	52	236
1	-4	123	116	325
1	-3	134	123	288
1	-2	69	55	132
1	-1	66	69	258
1	0	33	22	315
1	1	27	27	302
1	2	108	105	145
1	3	78	78	65
1	4	90	78	257
1	5	35	33	239
1	6	74	69	175
1	7	21	27	135
1	8	67	66	2
1	9	59	58	318
1	10	32	29	21
1	11	55	54	139
1	12•	33	5	257
1	13•	31	27	219
1	14	47	43	232
1	15•	25	36	118
2	-15•	27	18	239
2	-14•	31	37	12
2	-13•	34	42	75
2	-12•	36	5	34
2	-11	65	51	227
2	-10	51	34	147
2	-9	27	14	134
2	-8	45	42	78
2	-7	37	36	210
2	-6	48	42	60
2	-5	49	39	234
2	-4	78	71	4
2	-3	101	108	243
2	-2	21	11	294
2	-1	49	41	147
2	0	61	58	59
2	1	58	52	170
2	2	138	132	138
2	3	54	55	25
2	4	29	13	149
2	5	123	124	337
2	6	25	17	267
2	7	27	25	336
2	8	73	56	280
2	9	82	77	231
2	10•	28	29	30
2	11	94	112	123
2	12	52	53	48
2	13•	34	36	186
2	14•	31	33	287
2	15•	27	26	186
3	-15•	40	23	299
3	-14•	46	8	237
3	-13	69	57	204
3	-12•	54	5	310
3	-11	44	21	100
3	-10	250	267	53
3	-9•	42	15	129
3	-8	46	36	308
3	-7	367	386	239
3	-6	57	64	311
3	-5•	32	27	160
3	-4	232	259	62
3	-3	144	137	169
3	-2•	27	11	223
3	-1	38	39	257
3	0	61	63	7
3	1	52	50	294
3	2	52	62	275
3	3	56	62	192
3	4	64	45	116
3	5	58	61	138
3	6	70	64	14
3	7	64	38	295
3	8	76	69	295
3	9•	42	21	315
3	10	44	47	161
3	11	179	175	73
3	12•	54	40	175
3	13•	50	30	2
3	14	188	182	247
3	15•	40	26	1
4	-14•	29	28	48
4	-13	79	73	343
4	-12•	34	22	68
4	-11•	36	13	198
4	-10	111	128	173
4	-9•	28	22	325
4	-8•	27	40	269
4	-7	31	28	45
4	-6	42	53	200
4	-5	39	43	80
4	-4	116	137	346
4	-3	29	21	50
4	-2	39	44	171
4	-1	114	109	176
4	0	41	35	290
4	1	35	37	348
4	2	40	44	151
4	3	38	46	274
4	4•	21	9	227
4	5	26	39	280
4	6	34	56	169
4	7	52	68	135
4	8	60	75	8
4	9•	28	35	44
4	10	45	50	307
4	11	45	58	162
4	13•	32	16	45
4	14•	29	26	230
5	-14•	25	16	46
5	-13•	28	40	74
5	-12•	31	27	91
5	-11•	32	46	235
5	-10•	33	27	138
5	-9	68	69	200
5	-8	25	20	90
5	-7	63	70	242
5	-6	67	64	33
5	-5	85	89	55
5	-4	65	69	23
5	-3	20	19	292
5	-2	48	48	270
5	-1•	19	21	313
5	0	42	34	237
5	1	72	69	214
5	2	168	179	140
5	3•	20	20	260
5	4	65	85	55
5	5	120	142	316
5	6	23	45	94
5	7•	25	27	335
5	8•	25	17	220
5	9•	26	13	316
5	10•	33	42	227
5	11	71	74	117
5	12	31	28	270
5	13•	28	2	152
5	14•	25	32	328
6	-3	143	130	301
6	-2•	81	39	79
6	-1	93	87	251
6	0	182	195	123
6	1•	66	49	172
6	2•	81	34	218
6	3	135	125	317
7	-3	120	118	73
7	-2•	87	60	178
7	-1	79	98	154
7	0	36	19	350
7	1•	71	18	249
7	2•	87	19	335
7	3	102	97	238
8	-3•	61	38	11
8	-2•	94	44	216
8	-1•	76	28	338
8	0	58	53	195
8	1•	76	38	273
8	2•	94	54	167
8	3•	61	22	147
9	-3	164	180	284
9	-2•	98	31	17
9	-1•	83	57	246
9	0	263	276	116
9	1•	80	72	175
9	2•	98	24	135
9	3	154	177	304
10	-3	64	69	65
10	-2•	101	19	147
10	-1•	83	32	193
10	0•	41	36	17
10	1•	83	24	192
10	2•	101	37	264
10	3	64	68	200
11	-3•	78	56	11
11	-2•	122	49	139
11	-1•	101	25	40
11	0	50	42	198
11	1•	101	41	314

• UNOBSERVED REFLECTION. FO IS MINIMUM OBSERVABLE
$ ABSORPTION CORRECTION UNRELIABLE

TABLE II-4 (continued)

H	L	FO	FC	PHI
11	2•	122	64	273
11	3•	78	28	113
12	-3	105	114	268
12	-2•	115	34	320
12	-1•	95	16	270
12	0	118	145	98
12	1•	95	48	154
12	2•	115	19	36
12	3	92	93	295
13	-2•	102	33	320
13	-1•	85	44	285
13	0•	42	24	330
13	1•	85	39	144
13	2•	102	25	197
14	-2•	84	55	93
14	-1•	70	50	72
14	0•	35	28	237
14	1•	70	42	328
14	2	96	109	264
K= 4				
1	-14•	142	22	108
1	-13•	151	51	119
1	-12•	158	58	333
1	-11	128	82	1
1	-10•	126	11	342
1	-9•	120	29	164
1	-8	193	164	179
1	-7•	104	54	325
1	-6•	97	20	271
1	-5	218	187	346
1	-4	236	219	224
1	-3	37	30	61
1	-2	130	124	181
1	-1	479	547	64
1	0	98	78	158
1	1•	46	20	331
1	2	369	438	247
1	3	142	137	321
1	4•	83	34	66
1	5	127	119	86
1	6	213	222	151
1	7•	104	55	251
1	8•	112	56	27
1	9	146	134	350
1	10•	126	44	36
1	11•	128	26	311
1	12•	158	38	196
1	13•	151	78	182
1	14•	142	38	167
2	-15•	24	10	269
2	-14•	27	38	228
2	-13	59	64	349
2	-12•	32	21	39
2	-11	57	59	76
2	-10	84	90	180
2	-9•	25	11	240
2	-8	24	31	229
2	-7	58	46	138
2	-6	29	22	3
2	-5	46	39	253
2	-4	151	163	343
2	-3	49	48	191
2	-2	77	82	33
2	-1	109	114	165
2	0	24	6	311
2	1	19	29	295
2	2	76	80	160
2	3	32	35	309
2	4	55	58	214
2	5	86	86	316
2	6	34	29	119
2	7	27	25	35
2	8	24	15	26
2	9•	25	21	171
2	10•	26	17	164
2	11	61	51	119
2	12•	32	33	338
2	13	30	29	295
2	14	40	48	217
2	15•	24	29	171
3	-14•	29	12	48
3	-13•	32	33	1
3	-12•	34	23	261
3	-11•	36	7	254
3	-10	95	99	125
3	-9	28	34	117
3	-8	41	46	193
3	-7	61	55	259
3	-6	24	24	33
3	-5	74	80	24
3	-4	61	60	324
3	-3•	20	13	324
3	-2	43	55	229
3	-1	92	97	115
3	0	38	33	207
3	1	31	38	159
3	2	79	67	152
3	3	33	18	64
3	4	30	34	7
3	5	50	47	341
3	6	51	62	288
3	7	31	16	347
3	8	74	65	318
3	9	46	47	116
3	10	41	49	180
3	11	141	133	129
3	12•	34	18	294
3	13•	32	31	357
3	14	43	49	310
4	-14•	42	11	217
4	-13•	47	31	148
4	-12•	51	16	183
4	-11•	54	18	127
4	-10•	44	27	76
4	-9•	44	8	326
4	-8	73	79	314
4	-7	61	69	5
4	-6•	39	9	31
4	-5	109	109	126
4	-4	269	262	227
4	-3	35	33	298
4	-2	32	28	203
4	-1	481	539	57
4	0	82	76	157
4	1	53	57	313
4	2	417	495	244
4	3•	33	27	335
4	4•	35	14	263
4	5	170	178	85
4	6	85	68	3
4	7•	41	36	104
4	8•	42	53	10
4	9	72	49	190
4	10•	44	16	179
4	11•	54	15	238
4	12•	51	11	30
4	13•	47	14	316
4	14•	42	47	156
5	-14•	27	21	255
5	-13	39	24	2
5	-12•	32	29	73
5	-11•	34	13	128
5	-10•	36	39	176
5	-9•	29	45	295
5	-8•	29	6	342
5	-7	65	78	150
5	-6	51	44	239
5	-5	54	44	54
5	-4	126	142	335
5	-3	44	48	88
5	-2	47	63	226
5	-1	62	60	139
5	0	35	41	52
5	1	23	25	131
5	2	60	62	117
5	3	84	88	250
5	4	25	40	311
5	5	66	75	293
5	6•	27	9	159
5	7	50	73	102
5	8•	29	10	148
5	9	32	26	78
5	10•	36	38	199
5	11•	34	23	59
5	12•	32	18	333
5	13•	29	50	324
5	14•	27	51	200
6	-13	45	15	312
6	-12•	28	41	262
6	-11•	30	33	295
6	-10	53	56	130
6	-9	38	45	132
6	-8•	27	22	232
6	-7	45	47	297
6	-6	60	51	259
6	-5	58	63	80
6	-4	24	18	325
6	-3	104	102	53
6	-2	32	18	300
6	-1	44	55	127
6	0	57	57	224
6	1	62	59	221
6	2	26	13	357
6	3	36	48	163
6	4	97	115	52
6	5	25	32	352
6	6	40	59	352
6	7	43	44	255
6	8	41	47	303
6	9•	33	14	108
6	10	61	55	197
6	11	86	90	132
6	12•	28	13	221
6	13•	25	33	14
7	-3•	60	34	298
7	-2•	92	35	297
7	-1	194	227	63
7	0	37	26	140
7	1•	75	38	323
7	2	195	210	250
7	3	89	74	121
8	-3•	63	13	354
8	-2•	97	94	206
8	-1•	80	39	210
8	0	67	82	59
8	1•	80	54	78
8	2•	97	17	37
8	3	69	64	242
9	-3	82	104	27
9	-2•	100	44	4
9	-1•	82	32	205
9	0	69	78	224
9	1•	82	96	200
9	2•	100	41	311
9	3•	64	62	148
10	-3•	78	8	94
10	-2•	123	52	299
10	-1	112	116	155
10	0	50	21	216
10	1•	101	20	235
10	2•	123	101	332
10	3	99	80	94
11	-3•	74	39	209
11	-2•	118	67	201
11	-1•	97	38	248
11	0	50	46	50
11	1•	97	66	52
11	2•	118	31	341
11	3•	74	30	285
12	-2•	107	52	352
12	-1•	88	37	201
12	0	44	29	218
12	1•	88	25	154
12	2•	107	23	327
13	-2•	91	45	315
13	-1	134	164	176
13	0	45	50	259
13	1•	76	14	196
13	2	141	151	1
14	-2•	66	24	210
14	-1•	57	25	267
14	0•	28	20	10
14	1•	57	27	64
14	2•	66	40	312
K= 5				
1	-13•	148	14	81
1	-12•	156	52	223
1	-11•	129	24	126
1	-10•	128	49	128
1	-9•	123	35	27
1	-8•	117	23	222
1	-7•	109	40	209
1	-6•	103	29	115
1	-5	96	50	312
1	-4	134	120	342
1	-3•	41	31	235
1	-2	78	69	143
1	-1	119	108	136
1	0	45	25	317
1	1•	51	17	268
1	2	89	81	126
1	3	56	53	44
1	4•	90	33	319
1	5	111	112	303
1	6•	103	76	189
1	7•	109	12	203
1	8•	117	20	124
1	9•	123	17	290
1	10•	128	53	89
1	11•	129	57	137
1	12•	156	17	59
1	13•	148	51	262
2	-11•	49	18	2
2	-10	144	131	217
2	-9	100	105	260
2	-8•	37	31	269
2	-7	35	41	322
2	-6	126	140	93
2	-5	66	53	201
2	-4	29	22	134
2	-3	73	71	294
2	-2	139	133	20
2	-1	66	49	55
2	0•	27	11	296
2	1	186	176	192
2	2	154	144	55
2	3	48	51	128
2	4	91	88	29
2	5	294	357	240
2	6	40	56	350
2	7•	35	33	226
2	8	236	339	68
2	9	39	48	175
2	10•	39	15	98
2	11	102	146	259
3	-14•	25	22	82
3	-13	28	41	16
3	-12	31	39	106
3	-11	44	52	229
3	-10	72	78	173
3	-9	43	60	289
3	-8	38	44	48
3	-7	25	21	122
3	-6	23	14	241
3	-5	36	31	18
3	-4	85	85	334
3	-3	64	68	94
3	-2	72	82	153
3	-1•	19	29	28
3	0	61	56	288
3	1	63	64	312
3	2	136	147	167
3	3	56	62	244
3	4	36	22	293
3	5	85	100	336
3	6	49	56	86
3	7	40	45	55
3	8•	25	24	53
3	9•	26	16	203
3	10•	33	22	181
3	11	37	36	154
3	12•	31	22	279
3	13•	28	34	234
3	14•	25	45	225
4	-14•	27	12	158
4	-13•	29	42	79
4	-12•	32	38	206
4	-11•	34	13	224
4	-10•	36	31	228
4	-9•	29	15	219
4	-8•	29	11	317
4	-7	52	47	161
4	-6	38	38	30
4	-5	60	60	57
4	-4	109	116	327
4	-3	24	30	225
4	-2	63	62	191
4	-1	126	125	135
4	0	60	56	100
4	1	43	44	253
4	2	63	60	138
4	3	62	50	278
4	4	67	64	49
4	5	73	94	327
4	6	51	51	84
4	7	39	32	353
4	8•	29	11	218
4	9•	29	30	305
4	10	45	62	200
4	11•	34	45	96
4	12•	32	27	172
4	13•	29	21	76
4	14•	27	10	183
5	-13	169	145	46
5	-12•	47	9	39
5	-11•	51	17	335
5	-10	103	93	219
5	-9	44	48	189
5	-8•	44	22	355
5	-7•	43	39	354
5	-6	131	125	5
5	-5	50	51	273
5	-4•	40	12	189
5	-3	106	81	200
5	-2	204	211	122
5	-1•	38	8	191
5	0•	34	9	80
5	1	227	217	309
5	2	113	98	52
5	3•	39	30	122
5	4	81	85	129
5	5	225	279	237
5	6	72	76	317
5	7•	43	21	111
5	8	227	276	62
5	9•	44	30	122
5	10•	54	14	321
5	11	109	116	249
5	12•	47	32	174
5	13•	43	26	250
6	-13•	28	18	21
6	-12	80	78	84
6	-11	68	62	236
6	-10	55	34	192
6	-9	39	46	275
6	-8	46	19	75
6	-7•	36	5	25
6	-6	32	43	221
6	-5	76	81	21
6	-4•	27	19	55
6	-3	74	71	78
6	-2	112	101	190
6	-1	36	27	0
6	0	62	57	346
6	1•	27	21	319
6	2	73	71	182
6	3	57	62	224
6	4	41	50	46
6	5	46	44	4
6	6•	29	15	29
6	7•	36	39	205
6	8•	36	24	351
6	9•	35	34	113
6	10•	34	30	115
6	11•	32	32	115
6	12	29	22	299
6	13•	28	57	293
7	-12•	25	16	277
7	-11	48	50	202
7	-10•	29	29	251
7	-9	51	53	195
7	-8	58	52	335
7	-7•	33	33	110
7	-6	56	48	64
7	-5	64	65	76
7	-4	74	75	324
7	-3	49	51	283
7	-2	44	34	199
7	-1	47	49	136
7	0	42	32	34
7	1	67	65	245
7	2•	25	14	176
7	3	66	75	180
7	4	55	46	72
7	5	26	58	346
7	6	63	76	54
7	7	65	62	31
7	8•	32	39	186
7	9	31	63	297
7	10	96	100	204
7	11•	27	30	24
7	12•	25	44	152
8	-3	64	44	153
8	-2	243	238	121
8	-1•	82	47	214
8	0	40	31	24
8	1	244	291	307
8	2•	100	68	56
8	3•	64	16	173
9	-3•	79	26	44
9	-2•	124	84	196
9	-1•	102	10	3
9	0•	50	16	100
9	1•	102	13	327
9	2•	124	46	273
9	3•	79	10	295
10	-3•	76	35	299
10	-2•	119	26	109
10	-1•	99	50	251
10	0	49	40	318
10	1•	99	39	318
10	2•	119	36	235
10	3•	76	86	152
11	-2	121	106	123
11	-1•	91	37	185
11	0•	45	32	3
11	1	162	143	300
11	2•	110	33	161
12	-2•	95	39	225
12	-1•	79	34	166
12	0•	39	58	135
12	1•	79	27	108
12	2•	95	80	295
13	-2•	75	22	51
13	-1•	63	79	265
13	0•	31	40	271
13	1•	63	42	333
13	2•	75	29	154
K= 6				
1	-13•	143	81	359
1	-12•	153	57	183
1	-11•	158	47	140
1	-10•	128	114	174
1	-9•	127	56	352
1	-8•	121	19	300
1	-7•	115	19	124
1	-6•	108	43	296
1	-5•	104	59	9
1	-4	98	75	8
1	-3	67	76	140
1	-2•	70	9	138
1	-1	57	47	309
1	0	28	21	43
1	1•	57	31	129
1	2	110	111	155
1	3•	46	28	322
1	4	98	81	308
1	5•	104	37	324
1	6•	108	56	151
1	7•	115	31	116
1	8•	121	57	11
1	9•	127	46	343
1	10•	128	37	338
1	11•	158	60	172
1	12•	153	34	216
1	13•	143	41	188
2	-11•	48	59	216
2	-10	65	60	109
2	-9	59	43	238
2	-8	38	24	73
2	-7	63	53	292
2	-6	90	92	31
2	-5	78	64	310
2	-4	35	33	242
2	-3	62	60	210
2	-2	56	46	171
2	-1•	29	21	180
2	0	54	50	156
2	1	68	62	127
2	2	148	147	114
2	3	74	71	341
2	4	75	82	338
2	5	102	120	330
2	6•	35	26	112
2	7	47	57	156
2	8•	38	49	235
2	9•	40	47	152
2	10•	40	34	311
2	11	68	99	120
3	-3	163	148	47
3	-2•	81	26	93
3	-1	66	68	252
3	0	172	201	238
3	1•	66	43	21
3	2•	81	27	244
3	3	172	167	60
4	-13	59	56	356
4	-12•	28	21	192
4	-11	41	45	219
4	-10	71	72	173
4	-9	38	35	24
4	-8•	27	6	272
4	-7	33	20	56
4	-6	65	76	278
4	-5	54	66	37
4	-4	48	48	6
4	-3	112	114	130
4	-2	37	39	215
4	-1	23	12	129
4	0	59	55	336
4	1	53	49	193
4	2	23	17	229
4	3	51	62	298
4	4	65	63	8
4	5	25	31	214
4	6	46	57	133
4	7	57	66	136
4	8	62	75	8
4	9•	33	33	29
4	10	48	46	298
4	11	45	42	170
4	12	28	48	233
4	13•	25	4	110
5	-13•	28	5	288
5	-12•	29	12	95
5	-11	46	45	227
5	-10	60	50	107
5	-9	43	57	221
5	-8•	36	15	292
5	-7	35	28	287
5	-6	58	74	47
5	-5	92	109	26
5	-4•	27	17	320
5	-3•	27	9	303
5	-2	107	113	191
5	-1	29	25	287
5	0	57	49	207
5	1	36	24	177
5	2	103	106	126
5	3	27	20	29
5	4	94	100	7
5	5	102	104	311
5	6•	29	7	59
5	7	48	65	173
5	8	36	24	113
5	9	50	30	64
5	10	34	34	217
5	11•	32	38	126
5	12	45	37	289
5	13	36	29	31
6	-12•	42	9	74
6	-11	103	87	280
6	-10	77	76	29
6	-9•	52	2	237
6	-8•	44	39	35
6	-7	138	142	231
6	-6•	44	36	351
6	-5•	44	23	160
6	-4	158	172	53
6	-3	43	17	314
6	-2	47	38	91
6	-1	94	77	246
6	0	123	98	185
6	1	43	32	135
6	2•	42	30	179
6	3	105	98	17
6	4	167	177	301
6	5•	44	37	25
6	6	44	38	234
6	7	197	216	120
6	8•	44	54	256
6	9•	52	20	172
6	10	133	131	307
6	11	81	63	81
6	12•	42	30	86
7	-11	61	61	230
7	-10•	30	11	253
7	-9•	33	34	86
7	-8	48	37	38
7	-7•	35	10	216
7	-6	56	55	264
7	-5	39	28	31
7	-4•	29	10	278
7	-3	70	68	118
7	-2	39	38	177
7	-1	43	46	76
7	0	62	59	10
7	1	75	68	232
7	2	43	41	296

• UNOBSERVED REFLECTION. FO IS MINIMUM OBSERVABLE
& ABSORPTION CORRECTION UNRELIABLE

TABLE II-4 (continued)

H	L	FO	FC	PHI
7	3	61	45	258
7	4	107	112	23
7	5	44	45	157
7	6•	36	18	146
7	7	51	57	159
7	8•	34	33	8
7	9•	33	17	67
7	10•	30	40	234
7	11	39	16	231
8	-10•	26	12	141
8	-9	43	41	199
8	-8	56	46	200
8	-7•	31	25	341
8	-6	47	39	100
8	-5	79	73	13
8	-4•	33	9	96
8	-3	47	45	345
8	-2	88	80	175
8	-1	27	10	271
8	0	39	38	219
8	1•	27	27	337
8	2•	27	20	215
8	3	47	39	99
8	4	49	52	14
8	5•	33	19	25
8	6	32	22	306
8	7•	31	38	173
8	8•	29	29	60
8	9•	28	28	350
8	10•	26	17	158
9	-3	76	100	232
9	-2•	120	23	298
9	-1•	99	15	221
9	0	59	100	64
9	1•	99	47	154
9	2•	120	18	104
9	3•	76	49	271
10	-2•	112	16	81
10	-1•	93	39	38
10	0	46	43	35
10	1•	93	43	208
10	2•	112	49	268
11	-2•	99	54	154
11	-1•	82	19	69
11	0•	41	26	246
11	1•	82	40	342
11	2•	99	71	251
12	-2•	80	34	297
12	-1•	67	25	49
12	0	84	115	31
12	1•	67	46	124
12	2•	80	13	286
K= 7				
1	-13•	139	18	112
1	-12•	148	83	236
1	-11•	156	83	7
1	-10•	129	8	63
1	-9•	128	38	29
1	-8	178	147	217
1	-7•	121	34	20
1	-6•	115	46	114
1	-5	172	165	38
1	-4	173	173	223
1	-3•	51	49	345
1	-2	95	85	190
1	-1	306	319	54
1	0	58	54	157
1	1•	63	36	330
1	2	260	292	248
1	3	120	121	260
1	4•	105	9	286
1	5	134	134	103
1	6	172	223	56
1	7•	121	31	175
1	8•	126	23	4
1	9	148	174	241
1	10•	129	59	45
1	11•	156	20	348
1	12•	148	53	99
1	13•	139	56	221
2	-10•	49	32	156
2	-9•	40	52	312
2	-8•	40	25	272
2	-7	77	71	178
2	-6•	37	24	319
2	-5•	35	16	53
2	-4	143	160	3
2	-3	71	71	137
2	-2	62	56	49
2	-1	70	59	172
2	0•	33	16	218
2	1	61	43	240
2	2	77	65	166
2	3	122	109	322
2	4	39	5	324
2	5	35	29	312
2	6	81	89	134
2	7	38	54	37
2	8•	40	64	4
2	9•	40	30	104
2	10	49	48	200
3	-3	57	34	65
3	-2•	87	65	238
3	-1	71	95	125
3	0	38	48	230
3	1•	71	52	188
3	2•	87	18	344
3	3•	57	42	10
4	-3•	60	46	323
4	-2•	92	46	311
4	-1	205	240	43
4	0	37	28	108
4	1•	75	44	331
4	2	167	197	229
4	3	60	59	253
5	-12•	25	17	158
5	-11	77	72	226
5	-10	29	18	19
5	-9	34	46	326
5	-8	36	32	24
5	-7	46	53	194
5	-6	27	20	167
5	-5	53	52	75
5	-4	57	53	2
5	-3	26	19	87
5	-2	51	48	225
5	-1	26	23	118
5	0	34	25	77
5	1	36	35	205
5	2•	25	16	37
5	3	63	64	300
5	4	39	43	349
5	5	34	55	234
5	6	51	50	174
5	7	56	64	69
5	8	48	62	46
5	9	46	45	37
5	10	65	73	217
5	11	27	28	263
5	12•	25	19	309
6	-11•	28	9	303
6	-10•	30	20	210
6	-9	49	43	110
6	-8	50	44	328
6	-7	35	33	71
6	-6•	36	20	270
6	-5	53	54	128
6	-4	59	58	320
6	-3	34	35	46
6	-2•	29	25	306
6	-1	41	51	152
6	0	59	47	239
6	1	99	90	200
6	2	32	26	30
6	3	45	51	98
6	4	118	132	24
6	5•	29	29	207
6	6•	35	27	352
6	7	40	52	211
6	8	34	36	306
6	9•	32	20	288
6	10	65	64	168
6	11	44	48	84
7	-10•	44	9	179
7	-9•	46	36	12
7	-8	221	202	299
7	-7•	51	45	2
7	-6•	53	29	215
7	-5	201	208	119
7	-4•	45	39	179
7	-3•	45	11	350
7	-2	91	86	308
7	-1•	45	50	25
7	0•	44	7	115
7	1•	45	28	287
7	2•	45	41	224
7	3•	45	4	147
7	4•	45	30	152
7	5•	54	42	32
7	6•	53	30	214
7	7•	51	40	13
7	8•	49	28	291
7	9•	46	15	323
7	10	75	67	155
8	-10$	34	22	319
8	-9•	29	10	347
8	-8	49	41	31
8	-7•	32	20	278
8	-6•	33	23	126
8	-5	53	32	39
8	-4	67	49	139
8	-3•	36	32	248
8	-2	69	59	211
8	-1•	37	12	329
8	0•	35	30	64
8	1•	37	32	30
8	2•	36	36	347
8	3•	36	19	351
8	4•	35	22	272
8	5•	34	37	212
8	6	54	55	179
8	7	40	47	75
8	8	38	71	72
8	9	49	41	355
8	10$	71	53	230
9	-8	63	47	333
9	-7	66	53	83
9	-6•	28	34	132
9	-5	68	58	129
9	-4	42	36	327
9	-3	61	53	300
9	-2	54	39	345
9	-1	53	49	225
9	0	35	7	278
9	1	106	87	204
9	2	31	24	39
9	3	71	56	112
9	4	109	109	13
9	5•	29	16	153
9	6•	28	26	288
9	7	50	47	175
9	8•	27	20	72
10	-2•	101	87	307
10	-1	93	79	186
10	0•	42	31	267
10	1•	84	22	218
10	2	101	72	5
11	-2•	84	36	194
11	-1•	70	13	349
11	0•	35	25	39
11	1•	70	45	20
11	2•	84	35	302
K= 8				
1	-12•	143	51	206
1	-11•	151	32	174
1	-10•	157	29	70
1	-9•	129	34	316
1	-8•	128	45	6
1	-7•	126	28	236
1	-6•	122	71	44
1	-5•	118	43	298
1	-4•	113	59	337
1	-3	55	40	214
1	-2	85	67	136
1	-1•	69	74	160
1	0	43	39	146
1	1•	69	27	326
1	2•	85	38	87
1	3	105	109	310
1	4•	113	15	50
1	5•	118	80	298
1	6•	122	60	129
1	7•	126	54	272
1	8•	128	36	146
1	9•	129	35	114
1	10•	157	37	92
1	11•	151	12	123
1	12•	143	42	310
2	-9	193	196	245
2	-8•	40	44	320
2	-7	48	26	81
2	-6	211	252	56
2	-5	53	57	189
2	-4•	36	11	5
2	-3	148	129	232
2	-2	147	119	77
2	-1•	35	25	191
2	0•	36	4	353
2	1	147	135	272
2	2	130	93	54
2	3	45	38	86
2	4	77	59	55
2	5	174	190	230
2	6	78	80	329
2	7•	40	28	168
2	8	145	161	58
2	9	49	69	122
3	-3	109	97	117
3	-2	94	84	204
3	-1	76	57	348
3	0	58	64	322
3	1•	76	28	302
3	2•	94	52	154
3	3•	61	20	251
4	-3	69	68	249
4	-2	97	76	179
4	-1•	80	51	144
4	0	67	66	141
4	1•	80	39	322
4	2•	97	59	72
4	3	94	88	318
5	-3	64	64	241
5	-2	236	224	113
5	-1•	82	44	217
5	0	42	37	49
5	1	234	274	299
5	2•	100	87	28
5	3•	64	19	98
6	-10	29	31	358
6	-9	47	49	343
6	-8	43	27	210
6	-7	31	21	234
6	-6	32	24	185
6	-5	103	110	35
6	-4	51	29	153
6	-3	42	28	124
6	-2	93	97	209
6	-1	37	30	8
6	0	42	49	325
6	1	27	18	215
6	2•	27	13	302
6	3•	33	11	178
6	4	63	46	32
6	5	51	35	177
6	6•	32	26	122
6	7•	31	5	74
6	8	34	17	350
6	9•	28	20	245
6	10•	26	12	184
7	-10$	37	22	167
7	-9•	29	22	221
7	-8	84	77	354
7	-7	32	33	68
7	-6	82	65	87
7	-5•	34	8	89
7	-4•	35	37	293
7	-3	88	70	287
7	-2	64	59	165
7	-1	37	25	252
7	0	35	5	136
7	1	60	40	345
7	2•	36	38	120
7	3•	36	34	123
7	4•	35	15	210
7	5•	34	34	348
7	6•	33	5	36
7	7	52	42	9
7	8	45	40	176
7	9	47	45	280
7	10$	130	81	191
8	-8•	46	24	55
8	-7•	46	10	65
8	-6	71	80	190
8	-5	130	102	288
8	-4•	50	31	3
8	-3•	52	31	330
8	-2	227	196	113
8	-1	54	38	194
8	0	47	28	39
8	1	213	202	295
8	2•	52	38	29
8	3•	52	3	246
8	4	150	124	134
8	5•	49	6	57
8	6	62	25	185
8	7	46	58	2
8	8	98	49	271
9	-7$	37	37	248
9	-6	37	35	157
9	-5	82	63	48
9	-4•	31	28	121
9	-3	35	40	267
9	-2	70	65	221
9	-1•	34	23	99
9	0•	30	14	49
9	1•	34	15	53
9	2	68	49	311
9	3•	32	31	30
9	4	34	44	353
9	5	37	24	162
9	6•	31	47	171
9	7$	47	42	173
10	-5$	34	6	145
10	-4	77	52	87
10	-3	45	27	316
10	-2•	28	21	188
10	-1	99	69	281
10	0	45	49	273
10	1	64	47	7
10	2	50	51	163
10	3	82	74	96
10	4	56	27	197
10	5$	60	48	26
K= 9				
1	-12•	140	61	185
1	-11•	145	26	257
1	-10•	152	37	204
1	-9•	158	37	11
1	-8•	129	15	147
1	-7•	128	18	15
1	-6•	127	87	310
1	-5•	124	52	59
1	-4•	121	8	111
1	-3	145	145	143
1	-2•	92	33	306
1	-1•	75	31	302
1	0	63	59	0
1	1•	75	59	201
1	2•	117	50	161
1	3	59	52	279
1	4•	121	44	10
1	5•	124	37	24
1	6•	127	60	108
1	7•	128	22	91
1	8•	129	27	307
1	9•	158	27	7
1	10•	152	30	326
1	11•	145	16	185
1	12•	140	49	236
2	-8•	49	32	29
2	-7•	40	46	330
2	-6•	40	61	15
2	-5	44	55	332
2	-4	60	44	223
2	-3	65	54	146
2	-2	97	90	192
2	-1	37	16	52
2	0	39	29	254
2	1	41	50	73
2	2	76	57	105
2	3	38	26	355
2	4	94	90	325
2	5	39	71	280
2	6•	40	17	247
2	7	62	73	148
2	8•	49	19	220
3	-3	164	195	60
3	-2•	98	31	140
3	-1•	80	48	265
3	0	244	283	240
3	1•	80	54	18
3	2•	98	32	134
3	3	208	211	64
4	-3•	64	73	158
4	-2•	100	22	311
4	-1•	82	49	14
4	0	73	82	350
4	1	82	99	218
4	2•	100	24	265
4	3•	64	46	249
5	-3•	79	21	237
5	-2•	124	127	209
5	-1•	102	27	237
5	0•	50	29	318
5	1•	102	24	67
5	2•	124	43	51
5	3	79	38	88
6	-3	76	60	133
6	-2•	120	9	193
6	-1•	99	24	246
6	0	59	66	296
6	1•	99	33	97
6	2•	120	35	112
6	3	82	65	79
7	-8	28	9	340
7	-7	36	24	259
7	-6•	28	2	45
7	-5	29	13	47
7	-4	63	62	169
7	-3	50	34	224
7	-2	31	21	46
7	-1	79	72	39
7	0	49	47	25
7	1	88	78	220
7	2	62	62	277
7	3	46	38	214
7	4	85	75	37
7	5	52	48	130
7	6	28	23	137
7	7	33	27	212
7	8•	27	8	273
8	-7$	54	23	81
8	-6	40	31	139
8	-5	76	72	6
8	-4	34	30	348
8	-3	52	37	275
8	-2	80	73	192
8	-1	47	25	183
8	0•	30	19	325
8	1	44	32	26
8	2	49	14	323
8	3	49	39	111
8	4	41	44	359
8	5	40	31	167
8	6	31	7	47
8	7$	44	51	192
9	-5•	57	11	31
9	-4	70	25	263
9	-3	79	80	188
9	-2•	47	32	277
9	-1•	49	18	132
9	0	122	138	7
9	1	75	62	113
9	2•	47	12	134
9	3	95	92	188
9	4	104	86	296
9	5•	57	45	355
10	-2•	63	33	36
10	-1•	54	43	37
10	0	26	30	48
10	1•	54	25	219
10	2•	63	51	256
K= 10				
1	-11•	138	27	29
1	-10•	146	11	209
1	-9•	152	57	18
1	-8•	157	42	250
1	-7•	129	9	28
1	-6•	129	28	137
1	-5•	128	15	64
1	-4•	128	65	171
1	-3•	63	30	14
1	-2•	97	15	163
1	-1•	79	70	4
1	0•	39	22	88
1	1•	79	19	31
1	2•	97	51	221
1	3	134	151	247
1	4•	128	35	306
1	5•	128	46	98
1	6	202	250	60
1	7•	129	50	179
1	8•	157	29	314
1	9	205	216	240
1	10•	146	45	49
1	11•	138	6	303
2	-6•	49	24	63
2	-5•	40	54	85
2	-4•	40	15	312
2	-3•	40	27	134
2	-2•	40	46	314
2	-1•	40	21	323
2	0	51	45	200
2	1	97	78	216
2	2•	40	17	208
2	3	126	107	347
2	4	62	66	79
2	5	40	36	176
2	6	81	63	159
3	-3•	64	33	129
3	-2•	101	6	67
3	-1•	83	29	107
3	0	41	43	246
3	1•	83	56	179
3	2•	101	51	32
3	3•	64	49	8
4	-3•	78	7	206
4	-2•	123	47	332
4	-1	82	144	331
4	0•	50	40	80
4	1•	101	18	245
4	2	136	140	154
4	3	78	72	265
5	-3•	76	35	304
5	-2•	119	21	280
5	-1•	99	60	25
5	0•	49	25	228
5	1•	99	35	225
5	2•	119	30	352
5	3•	76	35	25
6	-2•	112	29	17
6	-1•	93	16	200
6	0•	46	5	329
6	1•	93	67	191
6	2•	112	33	83
7	-2•	101	78	304
7	-1	106	108	303
7	0•	42	23	48
7	1•	84	34	198
7	2	128	114	123
8	-5$	34	8	297
8	-4	81	54	182
8	-3	47	46	270
8	-2	37	30	155
8	-1	72	51	37
8	0	26	24	302
8	1	33	30	327
8	2	37	19	309
8	3	75	61	92
8	4	47	33	210
8	5$	71	60	201
9	-2•	63	31	350
9	-1•	54	22	254
9	0	38	36	65
9	1•	54	43	181
9	2•	63	20	95
K= 11				
1	-10•	138	48	35
1	-9•	146	42	294
1	-8•	151	81	30
1	-7•	156	13	68
1	-6•	159	45	90
1	-5•	130	69	237
1	-4•	129	48	191
1	-3•	64	41	268
1	-2•	100	39	134
1	-1•	82	9	326
1	0	63	69	134
1	1•	82	60	350
1	2•	100	57	4
1	3	103	110	323
1	4•	129	23	119
1	5•	130	53	216
1	6•	159	50	137
1	7•	156	15	285
1	8•	151	7	12
1	9•	146	43	140
1	10•	138	19	233
2	-5•	49	27	212
2	-4•	49	27	330
2	-3	155	127	238
2	-2	89	57	126
2	-1•	41	32	214
2	0	44	34	58
2	1	126	94	326

• UNOBSERVED REFLECTION. FO IS MINIMUM OBSERVABLE
$ ABSORPTION CORRECTION UNRELIABLE

TABLE II-4 (continued)

```
H   L     FØ   FC PHI   H   L     FØ   FC PHI

2   2*   40   33    9
2   3*   40   30   52         K= 14
2   4    69   48  184
2   5    94   90  133   1  -5*  140   72  226
3  -3*   78   43   94   1  -4*  144   65  190
3  -2*  122   52  264   1  -3*  147   45  312
3  -1*  101   31  344   1  -2*  105   26   63
3   0    50   51  285   1  -1*   87   60   16
3   1*  101   15  245   1   0    43   45  137
3   2*  122   45   43   1   1*   87   31   56
3   3*   78   33  151   1   2*  105   31  345
4  -3*   74   50  285   1   3*  147   37  345
4  -2*  118   50  163   1   4*  144   24  217
4  -1*   97   24  359   1   5*  140   75  176
4   0*   48   56  136   2  -2*   96   43  247
4   1*   97   56    3   2  -1*   80    1  290
4   2*  118   44   57   2   0    41   37   71
4   3*   74   53  344   2   1*   80   71   44
5  -2   121  120   99   2   2*   96   45  294
5  -1*   91   32  201   3  -2*   84   33  329
5   0*   45   22   62   3  -1*   70   11  241
5   1   128  118  293   3   0*   35   57  253
5   2*  110   59  344   3   1*   70   26  186
6  -2*   99   43  233   3   2    84   81   36
6  -1*   82   22  338   4  -2*   66   27  106
6   0*   41   49  277   4  -1*   57   40    2
6   1*   82    4  284   4   0*   28   28  171
6   2*   99   42   28   4   1*   57   18   41
7  -2*   84   50  158   4   2*   66   21   72
7  -1*   70   45  299
7   0*   35   19  206         K= 15
7   1*   70   31   13
7   2*   84   37  128   1  -2*   88   17  283
                        1  -1*   73   24  221
      K= 12             1   0*   36   12    2
                        1   1*   73   19   13
1  -9*  141    8  148   1   2*   88   47   54
1  -8*  144   27  147   2  -2*   75   22  255
1  -7*  149   17  141   2  -1*   63   24  194
1  -6*  153   78  358   2   0*   31   29  353
1  -5*  157   29   98   2   1*   63   65   64
1  -4*  159   20  243   2   2*   75   72   16
1  -3   113  103  166
1  -2*  123   39  313         K= 16
1  -1*  101   31  286
1   0    57   59  342   1  -2*   61   41   18
1   1*  101   38  217   1  -1    74  123  295
1   2*  123   20   98   1   0*   26   57   37
1   3*   78   41  253   1   1*   53    1  147
1   4*  159   58   94   1   2*   61   98  119
1   5*  157   31   91
1   6*  153   60   77
1   7*  149   32  328
1   8*  144   58  239
1   9*  141   25  249
2  -3*   76   66  141
2  -2    94   82  214
2  -1*   50   12   43
2   0    60   46  300
2   1    57   62   52
2   2    62   67   27
2   3*   76   17  139
3  -3   119  113   65
3  -2*  115   18  195
3  -1*   95    8  240
3   0   113  117  248
3   1*   95   23   56
3   2*  115   46  130
3   3   102  102   68
4  -2*  107   33  347
4  -1*   88   44    4
4   0*   44   41    0
4   1*   88   64  223
4   2*  107   12  248
5  -2*   95   60  208
5  -1*   79   35  201
5   0*   39   47    7
5   1*   79   49   83
5   2*   95   89   33
6  -2*   80   26  240
6  -1*   67   22  137
6   0    84   83  344
6   1*   67   48  101
6   2*   80   33  129

      K= 13

1  -7*  141   19  214
1  -6*  146    7  214
1  -5*  149   56  212
1  -4*  152   85  116
1  -3*   74   25  191
1  -2*  117   29   29
1  -1   153  153  300
1   0    48   48   50
1   1*   97    8  208
1   2   145  109  121
1   3   130  116  244
1   4*  152   24  317
1   5*  149   14  287
1   6   185  153   63
1   7*  141   45  164
2  -2*  111   61  315
2  -1*   92   56   18
2   0*   45   46  196
2   1*   97   35  202
2   2*  111    8  327
3  -2*  102   44   99
3  -1*   85   32  345
3   0*   42   17   79
3   1*   85   18  233
3   2*  102   15  114
4  -2*   91   31  348
4  -1   134  173  301
4   0    49   61   55
4   1*   76   28  204
4   2   155  161  121
5  -2*   75   27   30
5  -1*   63   84   32
5   0*   31   33  252
5   1*   63   18  187
5   2*   75   24  299

* UNØBSERVED REFLECTIØN. FØ IS MINIMUM ØBSERVABLE
$ ABSØRPTIØN CØRRECTIØN UNRELIABLE
```

TABLE II-5.

Final atomic parameters at 20°C.

Atom	Number	x	y	z	Atom	Number	x	y	z
Se	1	0.933(2)	0.968(2)	0.428	N1	1	0.11	0.08	0.33
	2	0.604(2)	0.292(2)	0.569(2)		2	0.80	0.43	0.49
	3	0.264(2)	0.638(2)	0.559(2)		3	0.45	0.71	0.45
	4	0.283(2)	0.974(2)	0.862(2)		4	0.48	0.10	0.77
	5	0.941(2)	0.307(2)	0.857(2)		5	0.12	0.36	0.76
	6	0.606(2)	0.636(2)	0.857(2)		6	0.78	0.68	0.76
	7	0.269(2)	0.306(2)	0.148(2)		7	0.43	0.48	0.07
	8	0.940(2)	0.643(2)	0.140(2)		8	0.13	0.79	0.08
	9	0.610(2)	0.973(2)	0.146(2)		9	0.80	0.08	0.06
C	1	0.07	0.04	0.43	N2	1	0.12	0.04	0.51
	2	0.74	0.39	0.57		2	0.80	0.41	0.66
	3	0.40	0.67	0.55		3	0.44	0.65	0.63
	4	0.43	0.06	0.86		4	0.48	0.06	0.94
	5	0.08	0.35	0.85		5	0.13	0.35	0.94
	6	0.73	0.65	0.85		6	0.78	0.63	0.92
	7	0.39	0.41	0.15		7	0.44	0.44	0.24
	8	0.08	0.73	0.15		8	0.13	0.72	0.24
	9	0.75	0.04	0.15		9	0.80	0.03	0.23

Overall temperature factor = 4.6(1)

TABLE II-6

H	L	FO	FC	PHI
K= 0				
0	1	576	630	189
0	6	72	60	53
0	9	32	38	342
0	12	14	29	292
0	15	15	15	67
1	-16•	11	6	5
1	-15•	14	9	346
1	-14•	16	7	22
1	-13•	17	6	91
1	-12	30	32	285
1	-11•	14	15	265
1	-10•	13	10	262
1	-9	50	60	118
1	-8•	11	8	178
1	-7	17	17	101
1	-6	60	53	85
1	-5	39	36	187
1	-4	31	29	347
1	-3	197	191	277
1	-2•	5	5	24
1	-1•	4	20	162
1	0•	3	2	131
1	1•	4	6	337
1	2•	5	7	109
1	3	183	164	89
1	4	30	22	154
1	5•	8	15	248
1	6	42	52	258
1	7•	10	10	251
1	8•	11	21	358
1	9	49	42	285
1	10•	13	15	26
1	11•	14	18	100
1	12	33	24	45
1	13•	17	10	213
1	14•	16	10	259
1	15•	14	10	157
1	16•	11	4	159
2	-16•	11	7	281
2	-15•	14	4	257
2	-14•	16	5	102
2	-13•	17	15	56
2	-12	15	17	307
2	-11•	14	15	305
2	-10•	13	11	222
2	-9	37	32	85
2	-8	36	22	84
2	-7•	10	10	77
2	-6	40	40	109
2	-5	62	51	203
2	-4	76	69	8
2	-3	108	116	275
2	-2	36	27	358
2	-1	23	20	182
2	0•	5	10	68
2	1	28	33	334
2	2	33	23	225
2	3	136	139	81
2	4	70	77	156
2	5	88	79	1
2	6	48	54	287
2	7•	10	14	281
2	8	18	28	290
2	9	60	59	247
2	10•	13	6	12
2	11•	14	24	124
2	12	56	53	75
2	13•	17	6	171
2	14•	16	6	318
2	15•	14	4	291
2	16•	11	7	85
3	-16•	10	3	312
3	-15•	13	11	318
3	-14	56	45	255
3	-13•	17	18	195
3	-12•	14	15	128
3	-11	67	54	70
3	-10	82	83	59
3	-9•	13	21	11
3	-8•	12	8	195
3	-7	248	212	260
3	-6	110	91	331
3	-5	21	28	323
3	-4	228	196	77
3	-3	372	374	174
3	-2	71	79	223
3	-1	11	17	23
3	0	636	572	358
3	1	30	37	33
3	2	59	64	268
3	3	404	369	191
3	4	208	202	66
3	5	46	46	193
3	6	88	79	37
3	7	233	210	257
3	8	19	29	305
3	9	23	20	344
3	10	77	67	80
3	11	71	60	54
3	12•	14	16	260
3	13•	17	10	304
3	14	56	48	243
3	15•	13	10	57
3	16•	10	6	190
4	-16•	9	9	10
4	-15•	13	6	315
4	-14•	15	9	61
4	-13•	17	9	309
4	-12•	17	4	247
4	-11•	14	32	334
4	-10•	14	25	155
4	-9•	13	6	133
4	-8	36	32	208
4	-7	18	8	322
4	-6	53	39	113
4	-5	62	58	158
4	-4	97	82	335
4	-3	77	78	295
4	-2	41	49	11
4	-1	90	126	138
4	0	33	29	195
4	1	76	99	327
4	2	23	25	127
4	3	46	59	106
4	4	77	74	159
4	5	49	58	311
4	6	29	17	221
4	7	17	18	192
4	8	31	30	17
4	9•	13	11	272
4	10	21	34	347
4	11•	14	28	124
4	12•	17	10	68
4	13•	17	5	123
4	14•	15	13	272
4	15•	13	6	152
4	16•	9	7	203
5	-15•	12	6	283
5	-14•	14	4	38
5	-13•	16	19	46
5	-12•	17	10	42
5	-11•	14	17	319
5	-10•	14	9	206
5	-9•	13	9	172
5	-8	29	19	114
5	-7	30	20	239
5	-6	11	17	236
5	-5	58	42	173
5	-4	53	57	359
5	-3	27	45	12
5	-2	85	109	329
5	-1	24	28	258
5	0	24	22	39
5	1	13	37	280
5	2	75	76	155
5	3	21	35	219
5	4	58	77	134
5	5	58	51	344
5	6	18	19	309
5	7•	12	15	22
5	8	22	19	287
5	9•	13	11	323
5	10•	14	24	290
5	11•	14	23	118
5	12•	17	4	72
5	13•	16	4	182
5	14•	14	3	261
5	15•	12	6	184
6	-15•	11	10	7
6	-14	66	54	238
6	-13•	15	26	219
6	-12•	17	17	213
6	-11	71	55	65
6	-10	125	111	55
6	-9•	14	14	112
6	-8•	13	10	265
6	-7	210	194	232
6	-6	20	30	9
6	-5	11	8	329
6	-4	156	176	55
6	-3	78	95	250
6	-2	28	40	182
6	-1	66	60	269
6	0	109	110	100
6	1	44	36	248
6	2	16	28	279
6	3	67	101	274
6	4	156	174	37
6	5	37	48	128
6	6•	12	17	103
6	7	167	182	230
6	8	39	42	272
6	9•	14	10	170
6	10	86	89	69
6	11	42	65	58
6	12•	17	4	2
6	13•	15	21	292
6	14	52	52	232
6	15•	11	1	171
7	-14•	12	4	41
7	-13•	15	14	292
7	-12•	16	19	44
7	-11•	17	18	354
7	-10•	14	25	125
7	-9•	14	25	244
7	-8•	14	12	147
7	-7•	13	2	70
7	-6	23	40	202
7	-5•	12	25	146
7	-4	54	86	295
7	-3	54	79	32
7	-2•	10	14	313
7	-1	70	81	124
7	0	32	34	194
7	1	66	61	332
7	2	41	40	53
7	3	38	59	208
7	4	28	30	141
7	5	23	36	280
7	6	25	34	21
7	7•	13	27	157
7	8•	14	20	306
7	9•	14	18	28
7	10•	14	22	333
7	11•	17	17	117
7	12•	16	13	181
7	13•	15	8	70
7	14•	12	5	306
8	-14•	11	2	342
8	-13•	13	6	43
8	-12•	15	17	53
8	-11•	17	13	326
8	-10•	17	3	311
8	-9•	14	25	217
8	-8•	14	12	165
8	-7•	14	33	226
8	-6•	13	22	270
8	-5	42	46	109
8	-4	23	26	64
8	-3	44	53	27
8	-2	78	74	318
8	-1	29	30	319
8	0	20	10	66
8	1	31	16	197
8	2	45	37	174
8	3	59	80	213
8	4	21	40	109
8	5	37	47	282
8	6•	13	8	92
8	7•	14	28	341
8	8•	14	12	118
8	9•	14	36	11
8	10•	17	17	254
8	11•	17	5	157
8	12•	15	16	204
8	13•	13	3	115
8	14•	11	4	169
9	-13•	12	10	226
9	-12•	14	12	226
9	-11•	16	22	46
9	-10•	17	36	43
9	-9•	17	20	109
9	-8•	14	4	250
9	-7	71	89	229
9	-6	25	33	91
9	-5	23	16	245
9	-4	84	85	63
9	-3	190	172	292
9	-2	13	17	27
9	-1	55	53	245
9	0	286	282	117
9	1	45	39	192
9	2	12	14	67
9	3	200	181	310
9	4	74	87	27
9	5•	13	17	106
9	6•	14	35	165
9	7	52	77	220
9	8•	14	20	255
9	9•	17	13	138
9	10•	17	29	53
9	11•	16	22	48
9	12•	14	12	30
9	13•	12	8	284
10	-13•	10	7	273
10	-12•	13	15	44
10	-11•	14	6	171
10	-10•	16	7	82
10	-9•	17	15	227
10	-8•	17	10	315
10	-7•	14	4	210
10	-6	27	34	225
10	-5•	14	12	276
10	-4•	14	22	276
10	-3	61	71	31
10	-2	25	20	118
10	-1•	13	8	142
10	0	18	11	135
10	1•	13	3	26
10	2•	13	11	9
10	3	47	48	209
10	4	22	26	264
10	5•	14	11	247
10	6•	14	30	22
10	7•	14	14	148
10	8•	17	4	182
10	9•	17	15	0
10	10•	16	7	31
10	11•	14	8	176
10	12•	13	9	162
10	13•	10	4	6
11	-12•	10	13	44
11	-11•	13	7	350
11	-10•	15	8	6
11	-9•	16	22	213
11	-8•	17	15	193
11	-7•	17	11	266
11	-6•	18	12	296
11	-5•	14	8	35
11	-4•	14	31	114
11	-3•	14	20	42
11	-2	15	14	267
11	-1•	14	11	312
11	0•	14	7	101
11	1•	14	8	159
11	2•	14	24	278
11	3	22	34	211
11	4•	14	11	200
11	5•	14	10	133
11	6•	18	15	28
11	7•	17	10	14
11	8•	17	17	90
11	9•	16	24	7
11	10•	15	5	176
11	11•	13	13	279
11	12•	10	22	197
12	-11•	11	7	252
12	-10•	13	14	188
12	-9•	14	5	168
12	-8•	16	3	163
12	-7	44	31	12
12	-6	43	30	84
12	-5•	17	5	101
12	-4•	17	22	153
12	-3	125	107	292
12	-2	24	24	346
12	-1	29	27	257
12	0	188	169	122
12	1	23	26	184
12	2•	14	24	60
12	3	112	114	308
12	4•	17	8	228
12	5•	17	12	313
12	6	29	31	138
12	7	28	18	24
12	8•	16	5	108
12	9•	14	5	97
12	10•	13	11	232
12	11•	11	6	199
13	-10•	10	7	259
13	-9•	12	5	313
13	-8•	14	10	308
13	-7•	15	7	350
13	-6•	16	17	213
13	-5•	16	12	265
13	-4•	17	17	115
13	-3•	17	25	42
13	-2•	17	8	95
13	-1•	17	15	251
13	0•	17	9	232
13	1•	17	21	107
13	2•	17	5	195
13	3•	17	24	220
13	4•	17	23	267
13	5•	16	16	10
13	6•	16	14	36
13	7•	15	3	343
13	8•	14	8	164
13	9•	12	3	62
13	10•	10	8	109
14	-8•	11	8	193
14	-7•	13	8	292
14	-6•	14	5	12
14	-5•	15	19	317
14	-4•	15	19	139
14	-3•	16	4	85
14	-2	32	19	113
14	-1•	16	13	48
14	0•	16	2	58
14	1•	16	8	331
14	2•	16	30	281
14	3•	16	7	278
14	4•	15	18	244
14	5•	15	22	127
14	6•	14	3	174
14	7•	13	8	94
14	8•	11	11	75
15	-7	35	37	11
15	-6•	11	15	99
15	-5•	12	3	63
15	-4	48	27	179
15	-3	47	29	303
15	-2•	14	7	332
15	-1•	14	8	305
15	0	39	38	135
15	1•	14	4	145
15	2•	14	10	60
15	3	28	35	315
15	4	23	19	188
15	5•	12	10	261
15	6	17	15	129
15	7	33	27	12
16	-3•	11	8	113
16	-2•	12	4	305
16	-1•	12	16	276
16	0•	12	5	275
16	1•	12	17	121
16	2•	12	9	147
16	3•	11	6	252
K= 1				
1	-16•	16	6	4
1	-15	77	76	179
1	-14•	18	6	334
1	-13•	19	8	141
1	-12	124	129	3
1	-11•	20	8	272
1	-10•	20	13	27
1	-9	77	69	171
1	-8	113	99	121
1	-7•	20	18	329
1	-6	35	42	282
1	-5	194	182	310
1	-4	165	157	225
1	-3	90	73	107
1	-2	25	41	144
1	-1	186	186	59
1	0•	10	8	185
1	1•	12	8	267
1	2	129	117	249
1	3	325	326	349
1	4	22	31	47
1	5	80	80	76
1	6	374	381	177
1	7•	20	26	247
1	8•	20	8	30
1	9	262	286	3
1	10•	20	10	306
1	11•	20	24	275
1	12	96	86	202
1	13•	19	17	114
1	14•	18	8	107
1	15	17	11	104
1	16	28	16	299
2	0	54	51	322
3	0	31	37	302
4	0	57	51	173
5	0	43	39	250
6	0•	21	17	317
7	0	35	46	155
8	0•	22	20	9
9	0	28	27	224
10	0•	22	11	130
11	0	29	22	73
12	0	27	23	217
13	0•	22	17	267
14	0•	21	7	64
15	0•	20	13	190
16	0•	19	14	257
K= 2				
1	0	40	39	231
2	-15•	17	10	275
2	-14•	18	9	96
2	-13	50	72	62
2	-12	51	38	157
2	-11•	20	17	277
2	-10	57	55	243
2	-9	179	158	354
2	-8•	20	5	101
2	-7	33	33	328
2	-6	298	309	182
2	-5	53	57	100
2	-4	54	63	148
2	-3	218	204	6
2	-2	53	51	303
2	-1•	15	19	296
2	0	37	43	353
2	1•	15	27	242
2	2	149	145	44
2	3	17	29	228
2	4	141	113	322
2	5	256	249	233
2	6•	19	27	132
2	7	45	38	164
2	8	241	239	59
2	9	73	55	187
2	10•	20	12	170
2	11	97	85	257
2	12	87	79	356
2	13•	19	11	347
2	14•	18	12	158
2	15	47	45	180
3	0	55	64	167
4	0	29	34	63
5	0•	20	10	180
6	0•	21	5	108
7	0•	22	4	147
8	0•	22	16	134
9	0•	22	2	247
10	0	25	13	357
11	0•	22	11	354
12	0•	22	5	187
13	0•	21	4	169
14	0•	21	9	323
15	0•	20	3	139
K= 3				
1	0	17	26	327
2	0	36	41	38
3	-15•	16	6	318
3	-14•	17	10	314
3	-13	40	30	199
3	-12•	19	3	294
3	-11	33	18	136
3	-10	164	165	52
3	-9•	20	10	159
3	-8	39	30	325
3	-7	261	291	242
3	-6	54	52	314
3	-5•	19	19	151
3	-4	222	225	66
3	-3	134	120	170
3	-2•	17	11	242
3	-1	42	34	262
3	0	49	59	4
3	1	45	49	293
3	2	53	57	280
3	3	61	52	186
3	4	59	46	137
3	5	66	47	135
3	6	59	40	2
3	7	53	34	312
3	8	53	38	270
3	9•	20	6	331
3	10	33	23	148
3	11	136	104	55
3	12•	19	18	184
3	13•	18	10	349
3	14	97	79	238
3	15•	16	9	343
4	0	26	27	303
5	0	24	35	262
6	0	133	140	129
7	0•	22	18	332
8	0•	22	23	213
9	0	179	167	121
10	0•	22	11	9
11	0•	22	11	213
12	0	63	60	107
13	0•	21	3	336
14	0•	20	6	248
K= 4				
1	0	80	68	163
2	0•	19	4	292
3	0	20	21	206
4	-14•	17	5	183
4	-13•	18	11	163
4	-12•	19	14	216
4	-11•	19	6	140
4	-10•	19	18	40
4	-9•	20	11	3
4	-8	50	41	297
4	-7	46	36	7
4	-6•	19	8	68
4	-5	76	67	113
4	-4	213	215	229
4	-3	33	30	296
4	-2	30	28	179
4	-1	412	449	57
4	0	71	65	158
4	1	57	53	312
4	2	413	401	244
4	3•	18	31	315
4	4•	19	16	220
4	5	148	126	81
4	6	70	46	7
4	7	20	25	105
4	8	25	27	30
4	9	45	33	193
4	10•	19	4	172
4	11•	19	13	288
4	12•	19	8	28
4	13•	18	8	262
4	14•	17	11	130
5	0•	21	20	14
6	0	24	22	228
7	0	36	20	136
8	0	37	36	49
9	0	40	30	233
10	0•	22	9	233
11	0•	22	18	56
12	0•	21	11	253
13	0•	21	19	261
K= 5				
1	0•	20	22	334
2	0•	20	20	320
3	0	34	41	266
4	0	27	39	112
5	-13	59	57	59
5	-12•	18	5	21
5	-11•	18	10	24
5	-10	61	47	239
5	-9	38	37	195
5	-8•	19	14	326

• UNOBSERVED REFLECTION. FO IS MINIMUM OBSERVABLE
ABSORPTION CORRECTION UNRELIABLE

Observed and calculated structure factors at 20°C.

H	L	FO	FC	PHI
5	-7	25	16	9
5	-6	106	102	11
5	-5	42	32	247
5	-4•	19	11	171
5	-3	76	74	203
5	-2	148	140	115
5	-1•	19	2	2
5	0•	19	19	43
5	1	142	150	305
5	2	94	78	48
5	3	19	21	133
5	4	59	55	128
5	5	194	198	234
5	6	45	44	320
5	7•	19	16	133
5	8	170	164	63
5	9•	19	13	116
5	10•	19	15	341
5	11	63	56	253
5	12	30	13	188
5	13•	17	8	204
6	0	28	21	332
7	0•	22	8	156
8	0	22	24	28
9	0•	22	9	96
10	0•	22	8	263
11	0•	22	15	16
12	0•	21	11	111
13	0•	20	10	264

K= 6

H	L	FO	FC	PHI
1	0•	21	12	69
2	0	21	32	161
3	0	161	170	237
4	0	32	27	326
5	0	28	21	223
6	-12•	17	4	5
6	-11	45	32	297
6	-10	45	35	46
6	-9•	19	5	119
6	-8•	19	13	29
6	-7	86	81	235
6	-6•	19	14	328
6	-5	34	19	177
6	-4	102	100	54
6	-3	37	26	9
6	-2	34	34	83
6	-1•	19	42	249
6	0	84	81	194
6	1•	19	17	105
6	2•	19	12	176
6	3	73	79	20
6	4	113	109	292
6	5•	19	11	358
6	6	34	28	219
6	7	117	117	115
6	8	34	22	240
6	9•	19	4	82
6	10	66	57	303
6	11	43	27	61
6	12•	17	6	110
7	0	29	26	3
8	0	22	13	250
9	0	33	31	76
10	0•	22	15	42
11	0•	21	9	250
12	0	33	35	19

K= 7

H	L	FO	FC	PHI
1	0	39	38	154
2	0•	22	13	274
3	0	22	20	218
4	0	36	17	94
5	0•	22	8	49
6	0	25	16	241
7	-10•	17	5	183
7	-9	26	19	21
7	-8	86	89	299
7	-7•	19	17	14
7	-6	19	17	213
7	-5	96	103	125
7	-4•	19	15	194
7	-3•	19	4	20
7	-2	41	44	312
7	-1•	19	23	25
7	0•	19	5	37
7	1•	19	16	345
7	2•	19	13	242
7	3•	19	12	217
7	4•	19	15	186
7	5•	19	14	17
7	6•	19	7	95
7	7	28	11	0
7	8•	18	7	249
7	9	18	8	244
7	10	38	25	119
8	0•	22	13	86
9	0•	22	9	270
10	0•	21	11	282
11	0•	20	8	58

K= 8

H	L	FO	FC	PHI
1	0	22	11	141
2	0•	22	13	350
3	0	28	26	311
4	0	35	30	147
5	0	29	30	32
6	0	22	9	313
7	0•	22	5	199
8	-8•	17	3	41
8	-7•	18	2	141
8	-6	23	20	179
8	-5	47	41	287
8	-4•	19	16	357
8	-3•	19	14	287
8	-2	80	92	115
8	-1	19	16	191
8	0	21	18	40
8	1	82	94	300
8	2•	19	16	14
8	3•	19	10	234
8	4	59	49	130
8	5•	18	9	74
8	6•	18	9	159
8	7•	18	15	345
8	8	33	20	265
9	0•	21	4	57
10	0•	20	12	271

K= 9

H	L	FO	FC	PHI
1	0	28	23	11
2	0•	22	9	196
3	0	188	191	238
4	0	40	29	337
5	0•	22	7	329
6	0	28	39	270
7	0•	22	13	12
8	0•	21	3	315
9	-4•	17	20	262
9	-3	26	23	178
9	-2•	18	6	268
9	0	58	46	358
9	-1•	18	11	100
9	1	30	21	111
9	2•	18	3	249
9	3	34	27	184
9	4	38	35	295
10	0•	20	7	46

K= 10

H	L	FO	FC	PHI
1	0•	22	9	107
2	0	25	12	228
3	0•	22	15	252
4	0•	22	20	72
5	0•	22	10	238
6	0•	22	4	301
7	0•	21	14	32
8	0•	20	6	254
9	0•	20	2	26

K= 11

H	L	FO	FC	PHI
1	0	33	20	124
2	0•	22	19	48
3	0•	22	11	287
4	0•	22	16	134
5	0•	22	13	48
6	0•	21	10	253
7	0•	20	3	181

K= 12

H	L	FO	FC	PHI
1	0	22	13	338
2	0•	22	6	267
3	0	66	63	247
4	0•	21	7	336
5	0•	21	9	43
6	0	33	26	341

K= 13

H	L	FO	FC	PHI
1	0•	22	15	59
2	0•	21	16	213
3	0•	21	7	82
4	0•	21	21	46
5	0•	20	10	244

K= 14

H	L	FO	FC	PHI
1	0•	21	8	115
2	0•	21	17	70
3	0•	20	9	236
4	0•	19	3	149

K= 15

H	L	FO	FC	PHI
1	0•	20	6	165
2	0•	20	5	39

K= 16

H	L	FO	FC	PHI
1	0•	19	12	43

• UNOBSERVED REFLECTION. FO IS MINIMUM OBSERVABLE
ABSORPTION CORRECTION UNRELIABLE

by J. S. Stephens. The effects of correlations were ignored, save for those resulting from the trigonal symmetry, and to the choice of origin (the z co-ordinate of Se 1 was fixed throughout both refinements at 0.428, which centred the layer at about 0.5). The resulting bond lengths and angles will be presented and considered in detail in the Discussion.

Ferroelectricity.

Although the crystal structure found for selenourea is totally unrelated to that of thiourea, we chose to examine selenourea for the presence of ferroelectricity. A crystal belonging to the point group C_3 must necessarily have its dipole moment parallel to c. If the structure of such a crystal is close to an equivalent structure with this dipole moment reversed, so that small atomic displacements might take one into the other, we have the possibility of ferroelectricity, the ferroelectric axis being c. This situation exists in the selenourea structure, if we choose to call displacements of 1.8Å small. The relationship between these equivalent structures is exactly that between the twins already remarked as existing in large selenourea crystals; their nature will be described more fully in the Discussion.

Since we have determined the atomic arrangement within the selenourea crystal, we are in a position to estimate the spontaneous polarisation, P_s, for selenourea. This estimate, however, cannot be highly precise, because the contribution of any one molecule to the total dipole moment is very small (and is not always of the same sign), the Se-C axis being always nearly perpendicular to c. If we use the low temperature atomic co-ordinates and assume a dipole moment of about 5 Debyes for selenourea (the dipole moments of urea and thiourea are 4.56D and 4.89D respectively, Kumler and Fohlen, 1942), we obtain a value for P_s of 1300 e.s.u. (4×10^{-7} coulombs/cm^2.), with +c as the negative pole. Although this is an order of magnitude less than for thiourea it still represents a readily measurable polarisation. The observed pyroelectric and piezoelectric effects (Kondrashev and Andreeva, 1963) and the tendency of the crystals to collect and retain surface dust lend credence to the suggestion that the dipole moment is not vanishingly small, which it could well be within the errors of the structure determination.

To examine the possibility of ferroelectricity, several large crystals of selenourea were ground so as to produce smooth faces, perpendicular to c and about 0.3 cm. apart. These crystals were of uniform cross-section of about 0.1 cm^2.. Silver paste electrodes were applied to the ground surfaces.

The apparatus used for the ferroelectricity measurements follows the design of Diamant, Drenck and Pepinsky (1957). The proper operation of this bridge was checked with samples of triglycine sulphate, a known ferroelectric, prepared in the same way as above. The behaviour of selenourea was then examined from room temperature to -130°C, by the simple expedient of suspending the sample within the low temperature Weissenberg camera. No sign of ferroelectricity was detected at any temperature within this range.

CHAPTER III.

DISCUSSION.

Space group and lattice parameters.

I shall begin by remarking upon one curious feature of selenourea, namely the point group, C_3. According to Buerger (1956) no organic representative of this point group is known. Although a few examples do in fact exist (α-L(+)-menthol, Ramsay and Rogers, 1952; γ-glycine, Iitaka, 1958), this crystal symmetry is certainly a rare one.

The lattice parameters found for selenourea are here compared to the previously reported values.

a(Å)	c(Å)	c/a	Reference.	
15.285(5)	13.007(5)	0.8510(4)	20°C	This work.
15.201(5)	12.950(5)	0.8517(4)	-100°C	
15.37(7)	13.08(5)	0.851	Kondrashev & Andreeva.	
15.34(2)	12.99(2)	0.847	Perez Rodriguez et al.	

The results of Perez Rodriguez et al., which they claim to be more precise, are probably more accurate than those of Kondrashev and Andreeva, since the former calibrated their films with the diffraction pattern of a copper wire, while the latter make no mention of a film shrinkage correction, and assign errors of a magnitude to be expected for this effect. Indeed the present work is in excellent agreement with Perez Rodriguez et al. as far as the c axis length is concerned. The results suggest that their a axis length may be slightly in error, in view of the agreement of our value of the axial ratio (which is independent of shrinkage correction) with the Russian work. Measurement of this ratio on an uncalibrated film (that used for the low temperature lattice parameters) gave the result $c/a = 0.850_3$, which agrees with the previous value within the errors of the determinations.

The discussion of the thermal expansion coefficients will be reserved until after the description of the structure.

Molecular structure of selenourea.

The fractional co-ordinates listed in Tables II-5 and II-6 do, in fact, correspond to nine distinct selenourea (V) molecules per asymmetric unit. The bond lengths and angles for each such molecule, derived from the low temperature refinement, are shown in Table III-1.

However, in general, these would not be the best estimates

TABLE III-1

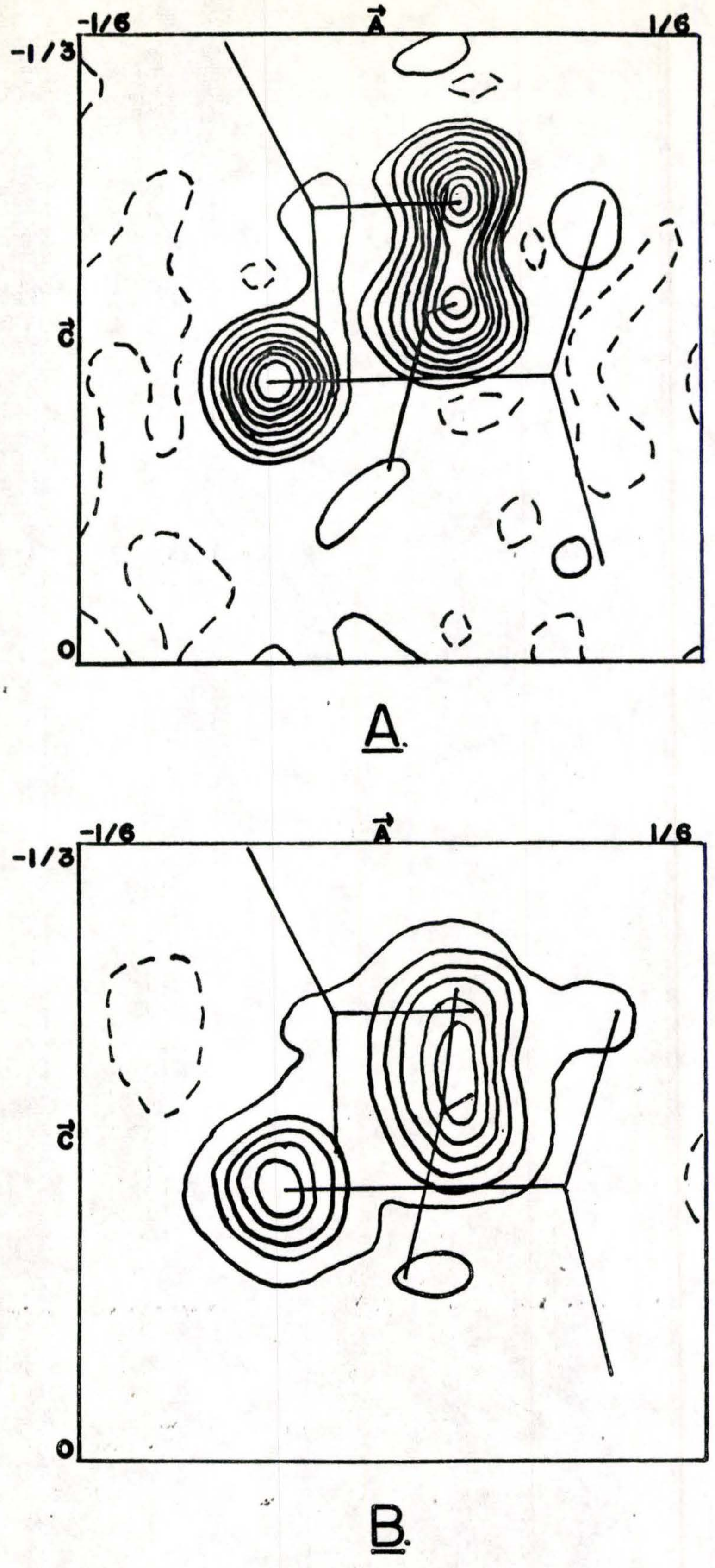
Dimensions of the individual selenourea molecules.

	Bond Lengths (Ångstroms)			Bond Lengths (degrees)		
Molecule	Se-C	C-N1	C-N2	Se-C-N1	Se-C-N2	N1-C-N2
1	1.85(8)	1.33(4)	1.34(7)	115(6)	118(6)	127(6)
2	1.86(7)	1.36(4)	1.36(7)	120(7)	131(8)	108(6)
3	1.94(9)	1.44(4)	1.37(6)	120(5)	111(5)	129(6)
4	1.83(8)	1.35(6)	1.39(4)	126(5)	113(6)	121(6)
5	1.91(7)	1.43(4)	1.38(4)	117(7)	119(6)	124(5)
6	1.83(7)	1.34(5)	1.28(6)	119(6)	128(7)	113(5)
7	1.84(11)	1.34(7)	1.35(7)	128(5)	121(6)	111(7)
8	1.87(11)	1.38(7)	1.36(7)	119(4)	119(5)	122(7)
9	1.83(11)	1.36(7)	1.35(7)	123(4)	115(5)	121(7)
Average	1.86	1.36		120		120

we could make of the molecular dimensions, since it is well known (see, for example, Grenville-Wells (1965)) that the main thermal motion of molecular compounds is libration about the centre of mass. Thermal motion has the effect of shortening the apparent bond length, but this can be corrected for (Busing and Levy, 1964) if the details of the motion are known. It is common practice in the particular case of rigid molecules (molecules without rotating groups) to ascribe as much of the motion as possible to translation and libration and correct for the latter (Cruickshank, 1956). In view of the reduction of this effect by use of low temperatures, and the high standard deviations both in the bond lengths themselves, and in the thermal parameters, this correction was not carried out, being insignificant and inaccurate.

The question now arises as to just how accurate an estimate of the molecular dimensions of selenourea can be made on the basis of this study. The improvement in resolution at low temperatures, discussed in the Introduction, is well illustrated by Figure III-1. Although this use of low temperatures and the three-dimensional data favour an accurate determination, the inherent inaccuracies of the intensity measuring technique, the problems in accurate refinement posed by pseudosymmetry and differences in scattering power as discussed in the Experimental, and the additional difficulties of lack of a centre of symmetry and the large number of parameters required to describe the structure, lead to standard

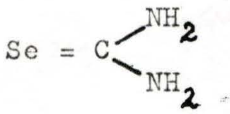
Figure III-1



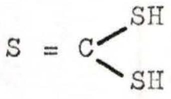
A portion of the electron density for selenourea projected on (010).
A. At -100°C. B. At 20°C.
Contours at $5e/A^2$, zero contour broken.

deviations in individual bond lengths which compare unfavourably with the more careful of current work. On the other hand we have in the crystal structure of selenourea a unique situation, certainly as far as molecular crystals are concerned, namely the presence of nine crystallographically distinct molecules in the unit cell.

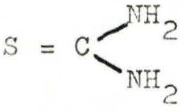
Kitaigorodskii (1961) notes that organic crystals containing crystallographically distinct molecules, although rare, are not unknown. However the majority of these contain only two distinct molecules, and, as far as I am aware, the previous record was held by trithiocarbonic acid (VI), (Krebs and Gattow, 1965) which contains 4 molecules in the asymmetric unit, 16 in the unit cell of space group $P2_1/a$.* The structure was determined by use of low temperature (-100°C) projection data, and did in fact show that



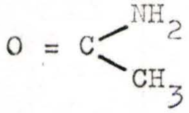
(V)



(VI)



(VII)



(VIII)

---

* 1:3:5-benzenetricarboxylic acid has 6 molecules per asymmetric unit, 48 per unit cell. D.J.Duchamp and R.E.Marsh (1965). Paper E8, A.C.A. Meeting, Gatlinburg, Tennessee.

the four molecules were essentially identical in structure. However Krebs and Gattow drew the dubious conclusion that the C-S single bonds were non-equivalent. This, and other studies of crystallographically distinct molecules, such as the low temperature structure of thiourea (VII) (Goldsmith and White, 1959) and the metastable orthorhombic modification of acetamide (VIII) (Hamilton, 1965), confirm the idea that the crystalline distortion of rigid molecules must be extremely small. Thus we can assume that an average molecular structure, based on all nine molecules, is a viable concept.

The structure, bond lengths and angles of this average molecule are displayed in Figure III-2. These are most conveniently compared with the low temperature structures of the analogues urea and thiourea, since in each case librational shortening of bond lengths is reduced. Goldsmith and White's values have been averaged over the two molecules. It is clear that the main difference is simply the increasing length of the C = X bond, and that the remainder of the molecule remains virtually identical throughout the series.

If we can now give support to the C = Se bond length quoted in Figure III-2, we can perhaps justify the choice of carbon positions used in the low temperature refinement. Figure III-3 shows suggested bond length bond order relationships for C-X bonds. If the single and double bond lengths are fitted by the Pauling

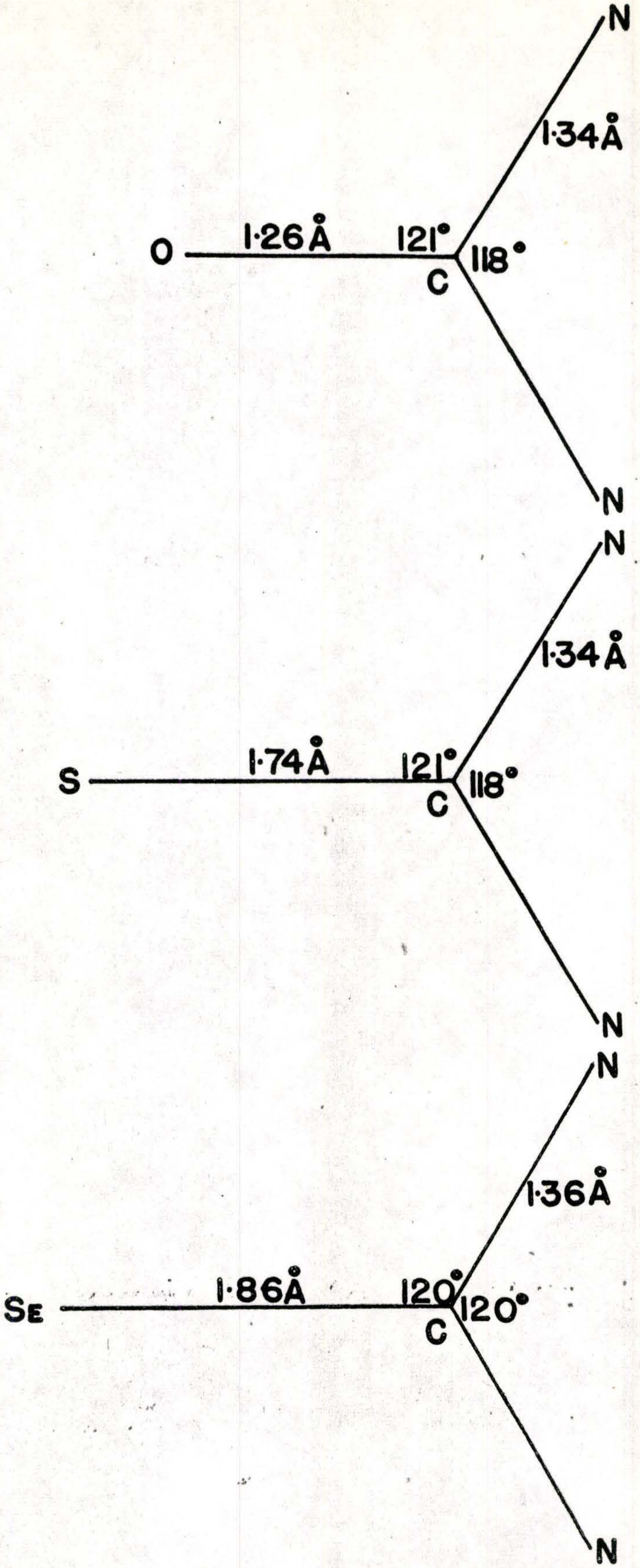


Figure III-2

Molecular geometries in the urea series.

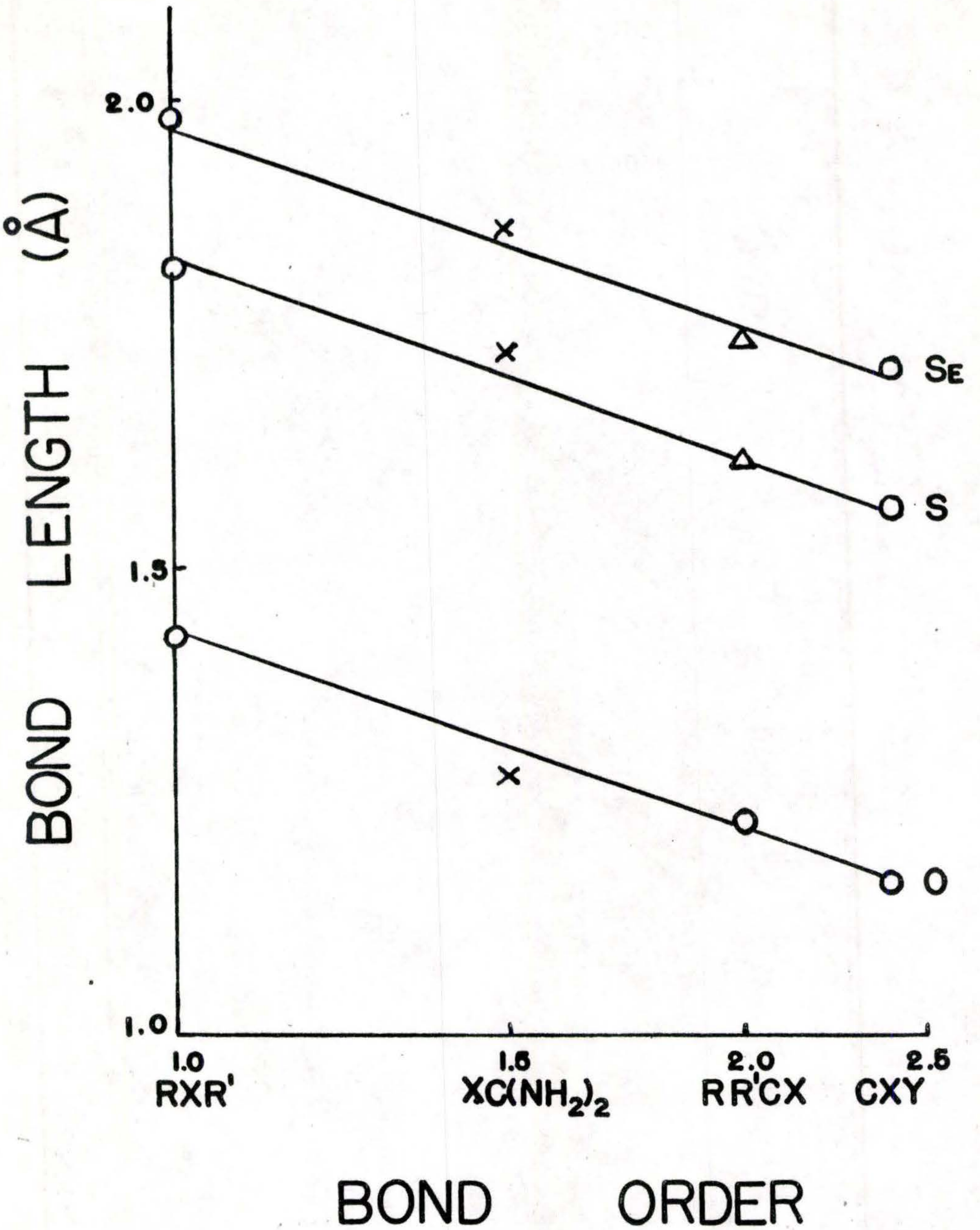


Figure III-3

Suggested bond order - bond length relationships for carbon - chalcogen bonds. (Semi-logarithmic plot).

× References of Figure III-2.
○ Average values listed in Sutton (1959).
△ Sum of covalent radii given in Pauling (1960).

(1960) expression

$$D(n) = D(1)-0.71 \log n \qquad \text{(III-1)}$$

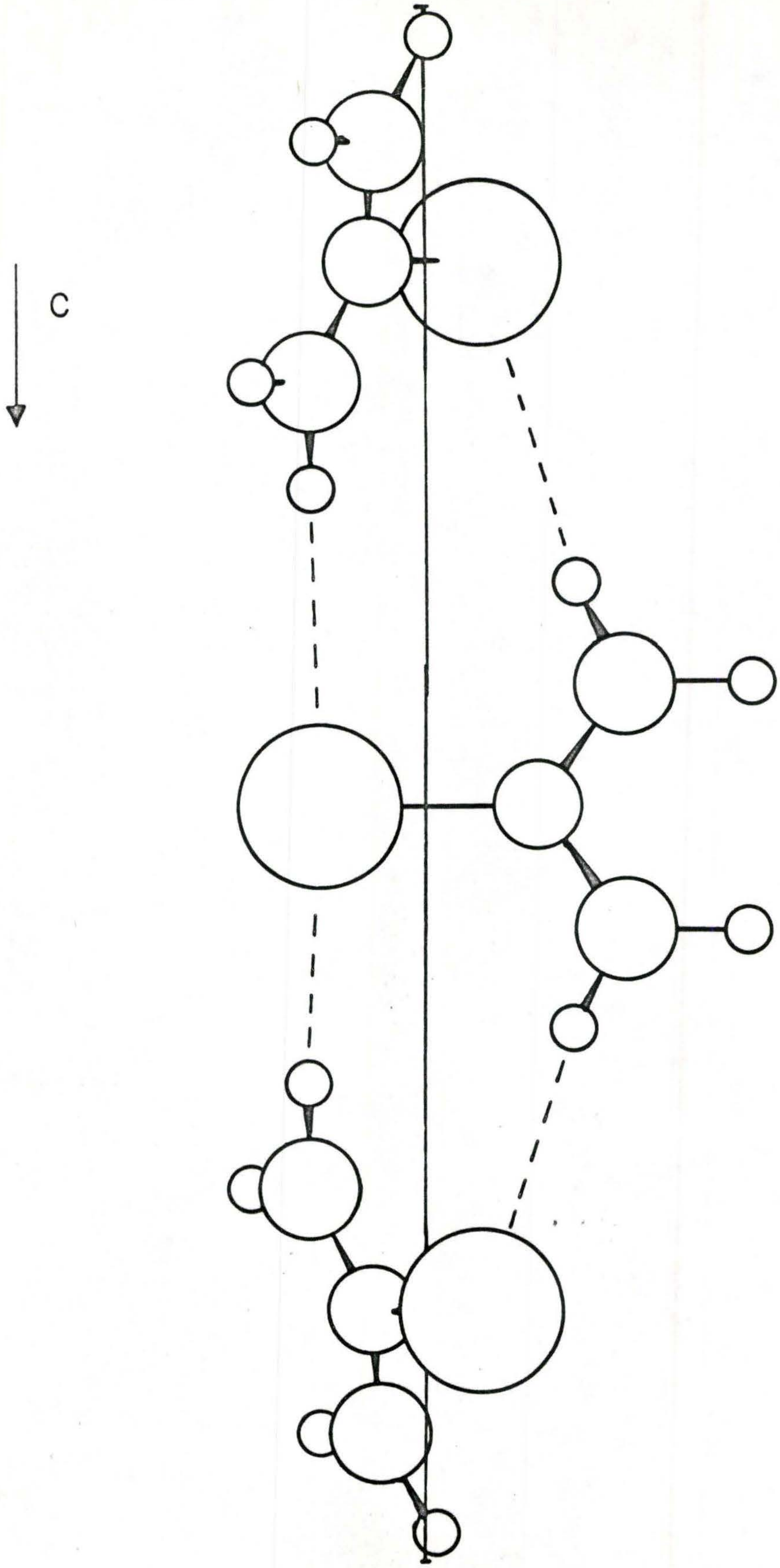
good agreement is found for CXY compounds assuming bond orders of 2.4. These graphs suggest C-X bond orders of about 1.5 throughout the urea series. The actual value is not so important as the support given to this determination by the identity of molecular structure found within the series. Unfortunately there seems to be no theoretical predictions of bond lengths in selenourea, and so we can only compare the experimental values to other members of the urea series, as done above, and to substituted selenoureas (Table I-2) with which the agreement is satisfactory.

Crystal structure of selenourea.

The unit cell of selenourea contains nine spiral chains. Each chain is essentially similar in form, since it contains three molecules and runs parallel to the c axis. A typical chain is shown in Figure III-4, which also illustrates the hydrogen bonding within the chain. Each molecule has one hydrogen atom directed towards the molecule above and similarly one towards the molecule below. In this respect they are similar to the spiral chains in the urea- and thiourea- hydrocarbon adducts discussed in the

Figure III-4

A typical chain in the selenourea structure.



Introduction. The relationship between these structures will be discussed in a subsequent section.

The distribution of the molecules within the chains is described in Table III-2. The symbols A, B, C and D refer to the detailed relative z co-ordinate of the particular chain; they fall naturally into these four groups each with a fairly constant separation, in alphabetical order, of 0.6Å. That is, the difference between A and D which distinguishes one subcell from the other two is about 1.8Å. These displacements are required to remove selenium atoms on neighbouring chains to their van der Waals contact distance of about 3.8Å. These contacts can be seen in Figure III-5, which also clearly shows the nine distinct spiral chains. The selenium atoms in contact form an approximately equilateral triangle within the layer, as do, for example, Se1', Se4 and Se7''. Three chains (those labelled A, D_1 and D_2 in Table III-2) spiral around the three distinct screw axes in the unit cell. The remaining six chains form two crystallographically equivalent sets, labelled B and C. Each of these chains contains three molecules unrelated by symmetry, yet each chain comes very close to containing the symmetry element 3_1, as can be seen in Figure III-5. The great similarity of these chains of unrelated molecules is even better illustrated by Figure III-6, which shows the structure projected down [$\bar{1}$10], in which case these chains come close to being superimposed. The A, B, C, D relationship can also be clearly seen in

TABLE III-2.

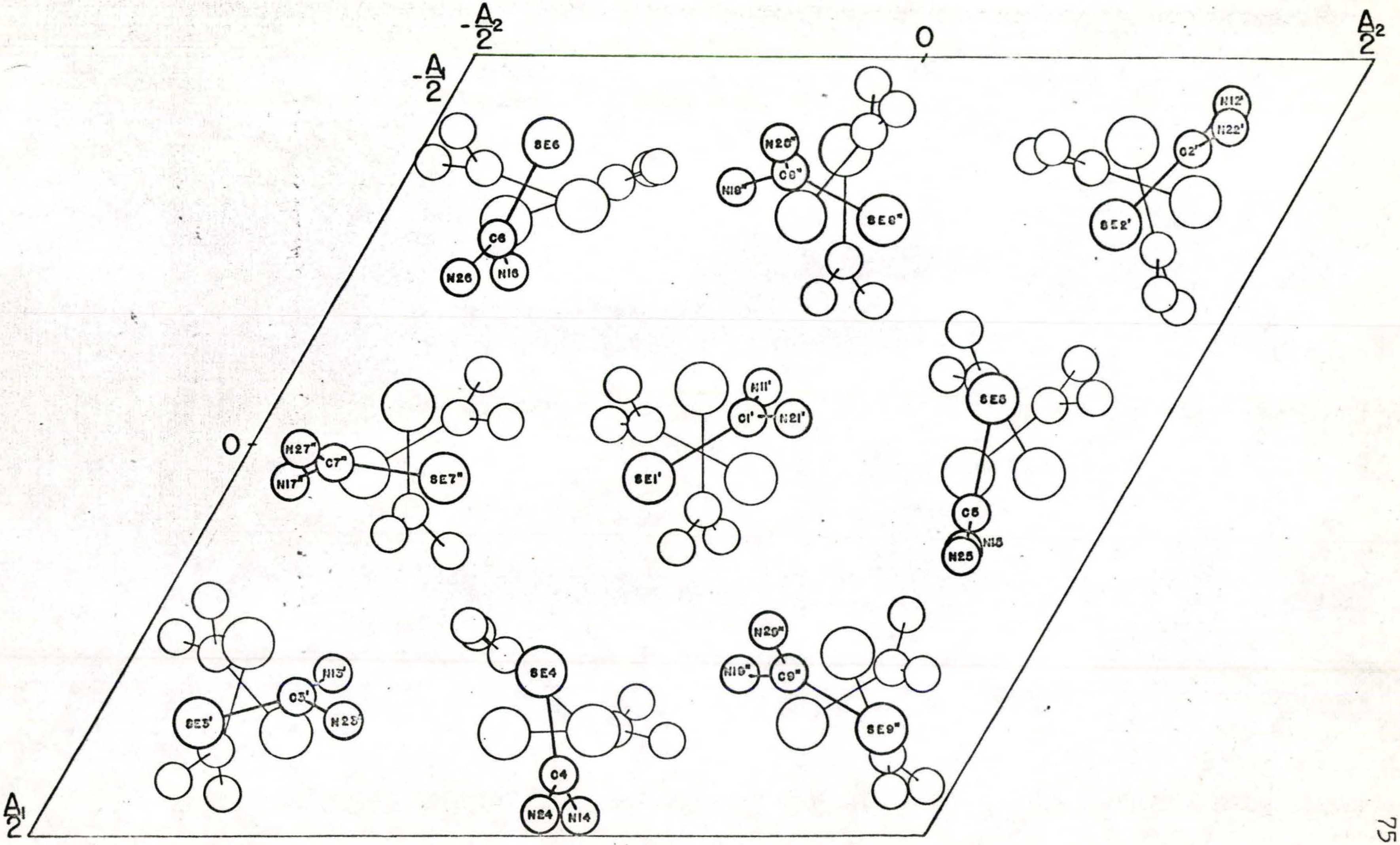
Distribution of molecules within chains in the selenourea structure.

Chain	Molecules
A	M1'' M1 M1'
B	M6' M5'' M4
C	M7 M8' M9''
D_1	M2'' M2 M2'
D_2	M3'' M3 M3'

The positions related by the elements of the space group $P3_1$ are denoted throughout as

X	x, y, z
X'	-y, x-y, z+1/3
X''	y-x, -x, z+2/3

Figure III-5.



The crystal structure of selenourea projected on (001).

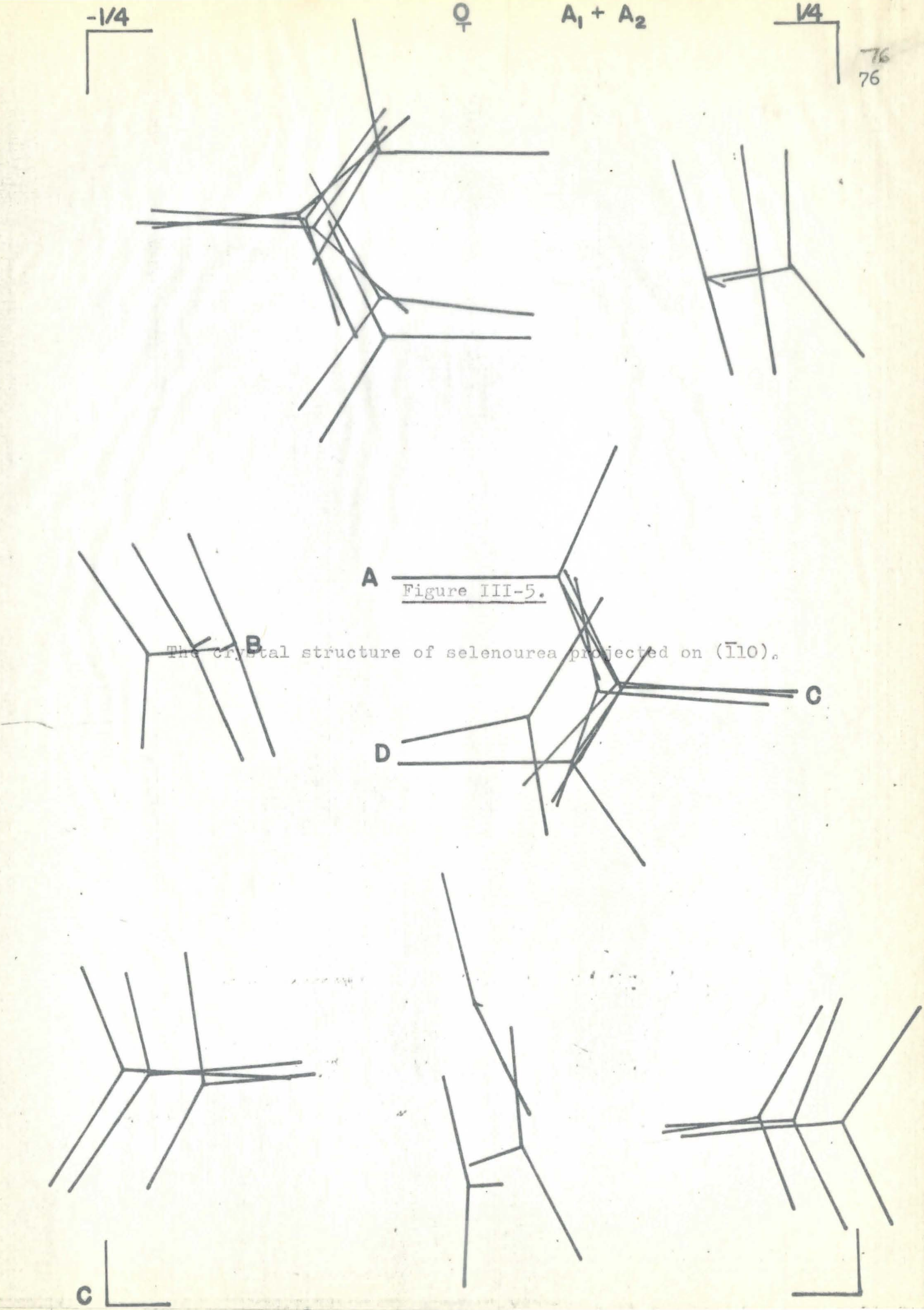


Figure III-5.

The crystal structure of selenourea projected on $(\bar{1}10)$.

this projection. As far as chains B and C are concerned the differences in z co-ordinate within the chain are only just significant. Distortions of similar magnitude seem to exist perpendicular to the chain direction, but these are difficult to estimate quantitively, since the chain axes themselves are displaced from their ideal positions. This is the result of slight relaxations of the structure to permit more efficient packing. The chain D_1 and its environment are rotated slightly counterclockwise, while the chain D_2 and the molecules surrounding it are rotated clockwise. This results in a slight lateral displacement of chains B and C.

Since each selenourea molecule has a remarkably similar orientation with respect to its chain axis, the existence of the hydrogen bonds within the chains is quite clear cut, their average length being 3.51Å.

The nature of hydrogen bonding between the chains is much more equivocal. We require the N...Se vector to be reasonable both in length and direction. The shortest distance of this type is N27''...Se5(3.46Å) which is similar in length to the intrachain hydrogen bonds. Distances up to 3.75Å (the longest intrachain bond length is 3.68Å) are listed in Table III-3B. These have been examined with respect to the second criterion, and the Table indicates which are proposed as hydrogen bonds. (The others are mainly between molecules in different layers as well as different chains). It can certainly be said that not all nitrogen atoms are involved in interchain

TABLE III-3

Intermolecular distances in the crystal structure of selenourea.

A. Intrachain hydrogen bonds.		
Se	N	Length (Å)
1	11'	3.31(2)
	21''	3.46(2)
2	12'	3.58(3)
	22''	3.55(2)
3	13'	3.24(3)
	23''	3.47(1)
4	16'	3.49(2)
	25''	3.54(2)
5	14'	3.51(2)
	26''	3.68(2)
6	15'	3.42(3)
	24''	3.54(4)
7	18'	3.50(3)
	29''	3.52(3)
8	19'	3.58(2)
	27''	3.58(3)
9	17'	3.58(2)
	28''	3.56(3)
Average		3.51

B. Other Se...N distances		
Se	N	Length (Å)
1	19'	3.66(5)
	29	3.70(4) *
2	24''	3.74(9)
	14	3.59(4) *
3	28'	3.61(7)
4	13'	3.64(7)
	23'	3.65(4)
	18	3.69(5) *
5	21'	3.62(7)
	17''	3.71(5)
	27''	3.46(7)
6	18''	3.60(7)
	17	3.70(4) *
	28''	3.74(7) *
7	16'	3.58(5)
	26'	3.70(5)
	25	3.72(3) *
8	26	3.66(3) *
9	15'	3.53(5)
	25'	3.73(4)
Average		3.64

C. Se...Se distances.			
Se	Se	Length at -100°C (Å)	Length at 20°C(Å)
1	4''	4.05(1)	3.99(5)
1	7'	3.57(1)	3.68(5)
4	7''	3.77(1)	3.79(5)
2	5''	3.55(1)	3.65(5)
2	8'	4.07(1)	4.01(5)
5	8''	3.71(1)	3.77(5)
3	6''	3.65(1)	3.68(5)
3	9'	3.69(1)	3.76(5)
6	9''	3.77(1)	3.78(5)
Average		3.76	3.79

*These distances are not considered to be hydrogen bonds and are not included in the average.

hydrogen bonds. Thus we have in selenourea a system in which the hydrogen bonds are so weak that some have been sacrificed in favour of compactness, that is, to gain energy by van der Waals interaction. The intrachain hydrogen bond lengths are listed in Table III-3A, and the short interchain N...Se distances are listed in Table III-3B, together with their interpretation in terms of hydrogen bonding.

Table III-3C contains the Se...Se contact distances, both at low and room temperatures. The average values are 3.79 Å at room temperature and 3.76 Å at -100°C. According to Pauling (1960) the van der Waals radius of selenium is 2.0Å. However, he chose this value in the nineteen thirties on the basis of a few structures, and recent work consistently suggests a smaller value. The distribution of 51 Se...Se distances all determined at room temperature cited in the literature* confirm a value of about 1.9Å. The shortening of these distances with temperature is of the order of magnitude to be expected for van der Waals contacts (see section on thermal expansion), and illustrates the care required in comparing intermolecular contacts at different temperatures.

---

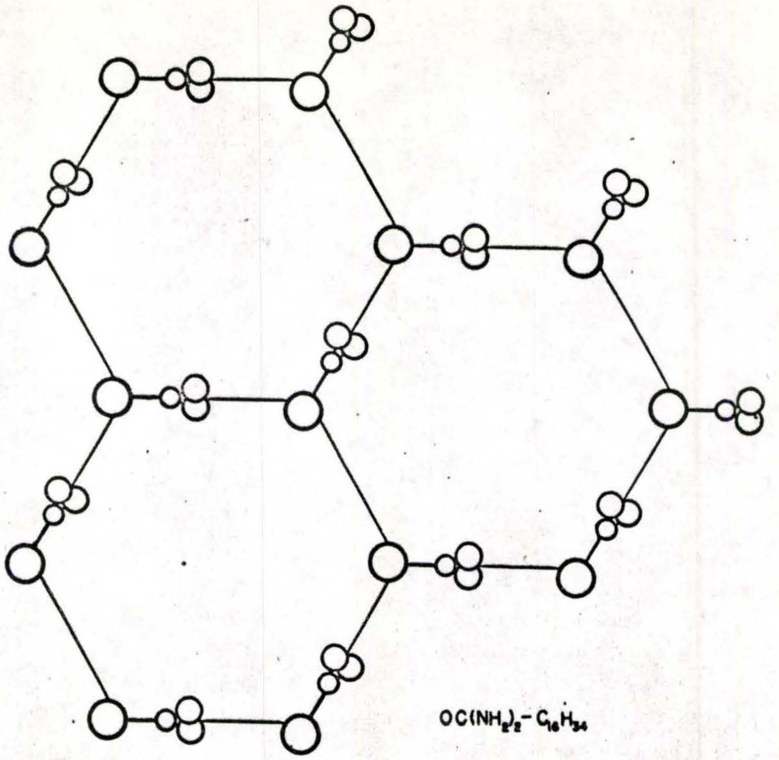
*Ketelaar, Hart, Moerel and Polder (1939), Burbank (1951), Marsh (1952), Marsh, Pauling and McCullough (1953), Tsernoglou (1966), Barnighausen, von Volkmann and Jander (1966).

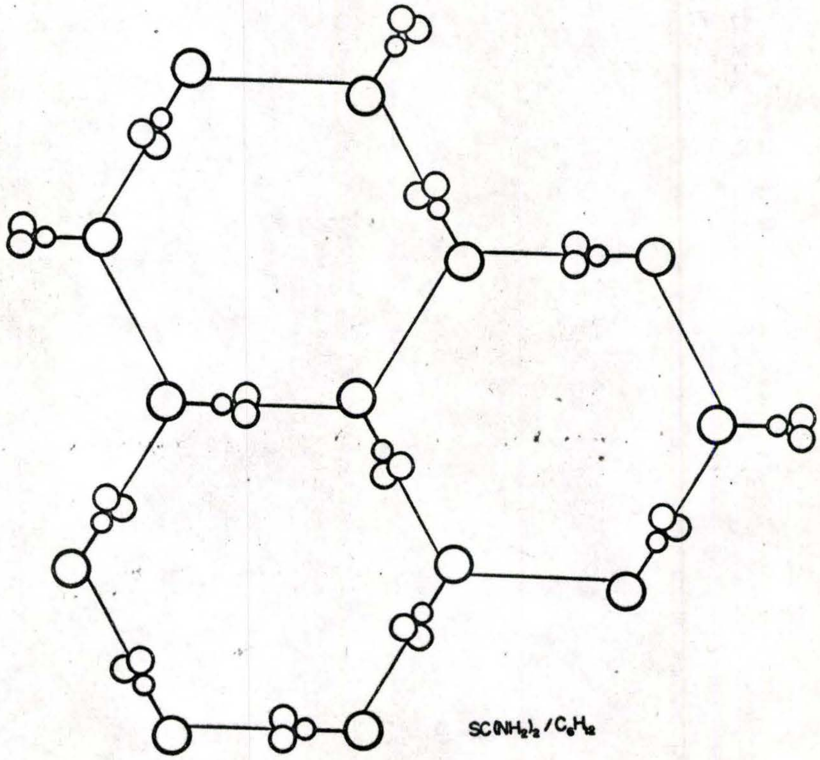
The three molecule chain in the urea series.

The three molecule hydrogen bonded chain occurs both in the inclusion compounds and in selenourea. The chains are so similar that the increase in c-axis length in the series is a direct measure of the increasing diameter of the chalcogen. However, the situation is complicated because direction of tilt of the molecules in the thiourea adduct is uncertain, although the angle involved is well determined, being about ten degrees. This arises because the sense of this tilt only has an effect on the $\ell \neq 0$ mod 3 structure factors, and even then the contribution is small. Lenné chose the direction to be opposite to that in the urea compounds, where the angle of tilt is about seven degrees, on the basis of slightly better agreement for the hkl layer line. Since the sense of tilt found in the urea compounds recurs in selenourea, where the corresponding angle averages seventeen degrees, this choice now forms a stumbling block to a comprehensive structural description of these compounds, which I shall nevertheless attempt to present.

When we attempt to draw further analogies between these structures, we find the mode of cross-linking of the chains differs for each compound. Figure III-7 is based on part of Lenné's paper, and represents a c/3 deep slice of the urea- and thiourea-hydrocarbon complexes projected on the (001) plane. Each spiral

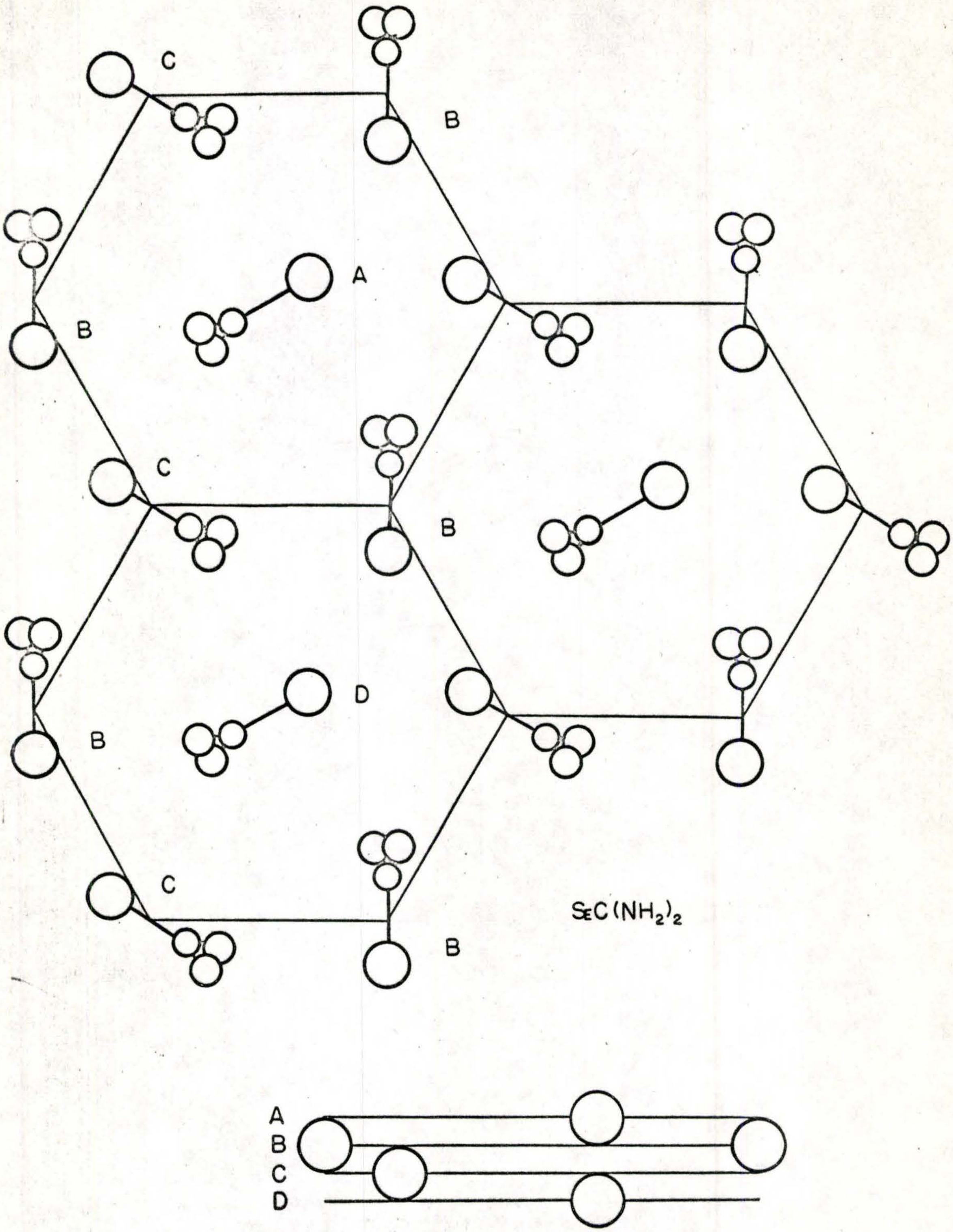
Figure III-7.





The crystal structures of the urea- and thiourea- hydrocarbon complexes.

Figure III-8.



The crystal structure of selenourea, idealised for comparison with Figure III-7.

contains a three-fold screw axis parallel to c. The urea and thiourea molecules form the honeycomb arrangement described previously and the hydrocarbon molecules, the honey, are left out for clarity. In these crystals the between chain hydrogen bonding from any molecule is to two oxygen (or sulphur) atoms on different molecules of the same adjacent chain. Alternate chains point in opposite directions in the (001) projection. The basic difference between the two inclusion compounds is that in the thiourea case alternate chains also have the opposite sense of screw, which imposes a centre of symmetry and a rhombohedral centering on the lattice.

If we compare Figure III-8, which represents a similar slice of the selenourea structure, we find that the individual chains have been rotated, so that all nine have an identical orientation in the (001) plane and differ only in z co-ordinate Thus all nine chains in selenourea stand in the same relationship to one another, and we cannot describe the structure by assigning a specific chain to the basic structure or to the channel. A further illustration of this rearrangement of the chain orientation in the (001) plane is provided by Figure III-9, where the a and c axis lengths for the three crystals are compared to the van der Waals radii (Pauling, 1960) of the corresponding chalcogens. This shows clearly that the increase in c axis length results simply from the greater chalcogen diameter. However the a axis lengths only

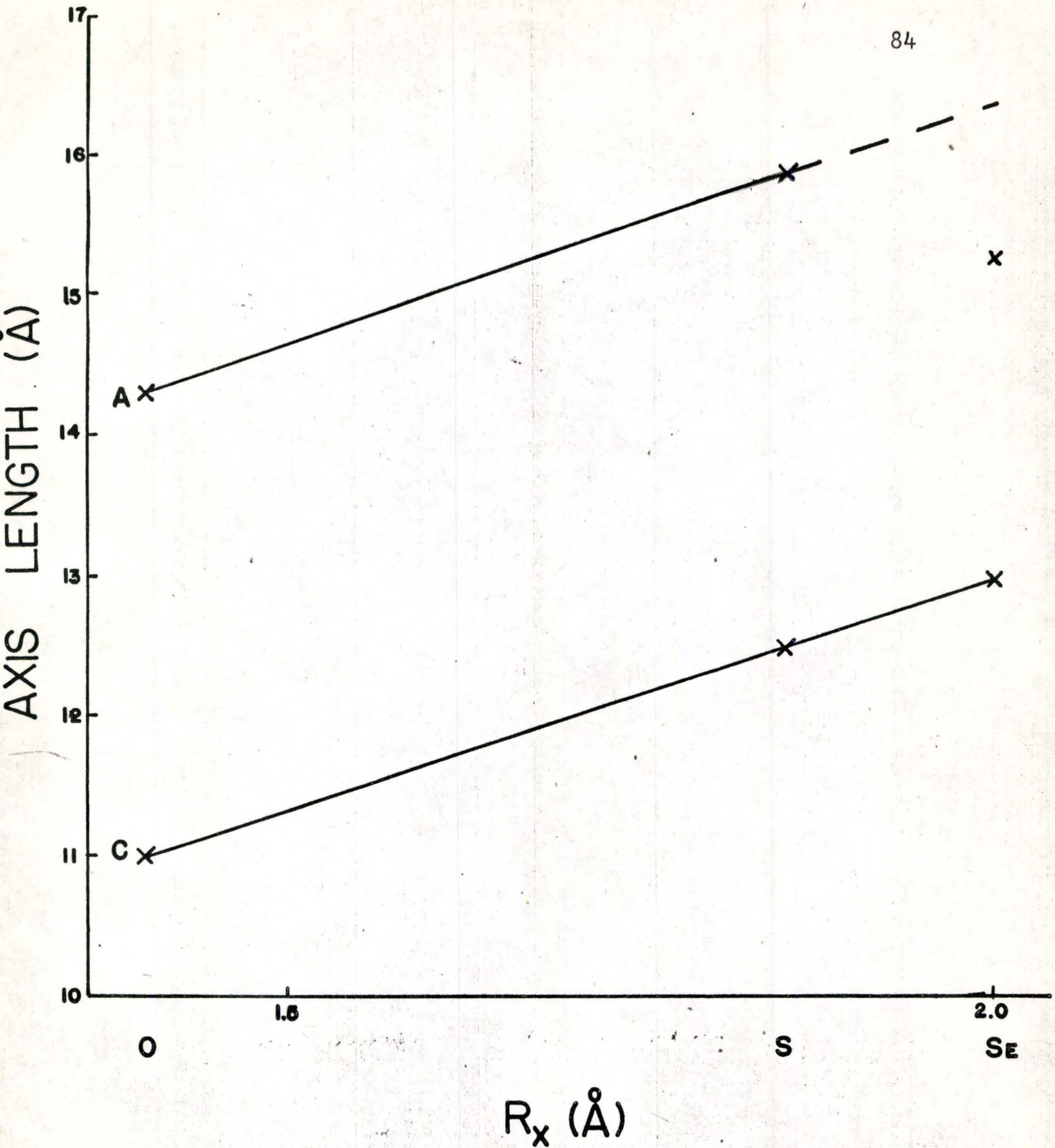


Figure III-9

The axis lengths in the spiral chain compounds compared to the corresponding chalcogen radii.

follow this trend for the inclusion compounds, whereas selenourea has a markedly shorter (by about one Ångstrom) a-axis than would have been expected based on an 18 molecule honeycomb structure. It therefore appears that the axial ratio is a reflection of the orientation of the chains in the (001) plane for all these compounds. In this connection it is interesting to note the report (Mima, 1959) that the thiourea/8-oxocamphor adduct ($C_{10}H_{14}O_2 \cdot 3SC(NH_2)_2$) has an axial ratio of 0.81, compared to the usual value of 0.774. This suggests the possibility of rotation of the chains, to allow hydrogen bonding to the oxygen atoms of the terpene.

Another aspect of the propensity of the urea series to form these three molecule spiral chains is the high solubility of thiourea in the selenourea structure. Crystallisation of a solution of both compounds in water yielded mixed crystals with the selenourea structure. These showed diffuse spots, near the Bragg reflections, which corresponded to the pure selenourea spacing (see Wooster, 1964). The Bragg reflections themselves corresponded to an apparently isotropic reduction in lattice parameter of one per cent, or a volume per molecule of 94.5Å^3. Since the corresponding values for the pure components are 90.3Å^3 (thiourea) and 97.4Å^3 (selenourea), this mixed crystal contains a large mole fraction, about 0.4, thiourea.

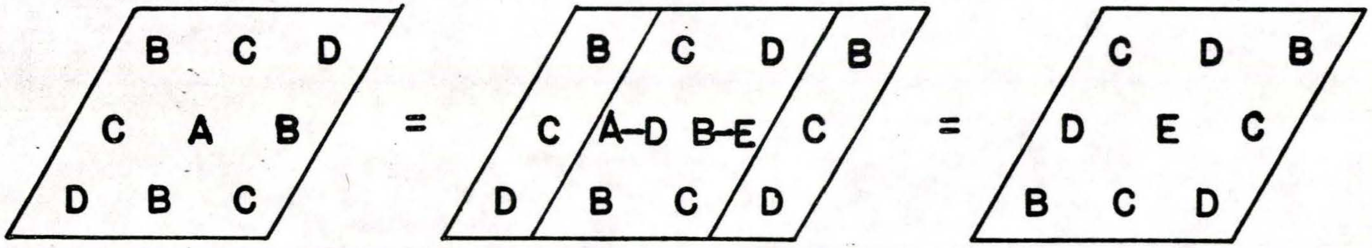
We can also calculate, considering the molecules to be 'hard', the volume of the voids in the crystal structure, and hence the efficiency of the packing in the crystal. Using the Kitaigorodskii (1960) formula, we can show that the molecular volume increase in going from thiourea to selenourea is 5.7Å^3. Since packing coefficients for molecular crystals are commonly about 0.65, we expect a crystal volume increase of about 9Å^3 (5.7/0.65). That the actual increase is less than this reflects the more efficient packing in the selenourea structure.

This expected increase of about 9Å^3 is close to that reported by Dvoryankin and Ruchkin (1962) for the orthorhombic modification (volume per molecule 99.7Å^3). If this thiourea-type phase exists for selenourea, then, if we accept Kitaigorodskii's arguments, we can predict it to be metastable with respect to the trigonal form.

Twinning in selenourea.

The relative z co-ordinates of the various chains in selenourea are indicated in Figure III-10, using the nomenclature of Table III-2. Figure III-10 also contains a similar description of the twin configuration, which can be considered as the same enantiomorph of selenourea rotated about [100] so that c becomes -c. (No attempt was made in this study to distinguish between the enantiomorphs represented by the space groups $P3_1$ and $P3_2$, which probably occur equally frequently. Instead $P3_1$ was assumed

Figure III-10



A hypothetical switching mechanism for selenourea, showing the structural relationship between the twins. The letters identify the individual chains according to the scheme of Table III-2.

throughout.) One of several possible transformations from one twin to the other are indicated, involving movement of two chains by about 1.8Å. This distance is large compared to that involved in known ferroelectrics, and such a movement of chains would require a gross change in the hydrogen bonding arrangement, so ferroelectricity is precluded. However, the similarity described encourages the production of such twins during the growth of crystals.

Thermal expansion of selenourea.

Thermal expansion coefficients for molecular crystals are of interest, in view of their relationship to the detailed crystal structure, particularly the strength and direction of interatomic interactions (Lonsdale, 1959). The magnitude of the thermal expansion coefficient α_x is related to the extent of anharmonicity of lattice vibrations propagating in the direction $\underline{x}$, which in turn depends on the strength of the interatomic interaction, whether covalent bond, hydrogen bond or van der Waals forces, and increases in the order just outlined. Some examples of the magnitudes involved are listed in Table III-4, together with the selenourea values.

Of particular interest to the present study are the thermal expansion coefficients for urea (Gilbert, 1955), the structure of

TABLE III-4.

Some typical coefficients of thermal expansion.

Substance	Temperature Range (°C)	$\alpha \times 10^6/^\circ C$	Bond Type
Diamond	23... 55	1	Covalent.
Ice	-120...-90	α_a 52 α_c 46	Hydrogen bonds.
Benzene	-193... -3	α_a 119 α_b 106 α_c 221	van der Waals.
Urea	-183... 20	α_a 76 α_c 24	Hydrogen bonds.
Selenourea	-100... 20	α_a 46 α_c 36	Hydrogen bonds.

which (see Introduction) is characterised by a fairly open arrangement of hydrogen bonds. They result from a large librational amplitude about the C-O bond axis, along with an increased vibration of all the atoms of the molecule perpendicular to its plane. This latter effect is found in general for planar molecules; in crystalline benzene, for example, the expansion in the c direction (almost perpendicular to the molecular plane) is about twice its value at right angles. Gilbert's conclusions were confirmed by the diffuse X-ray scattering for urea (Gilbert and Lonsdale, 1956). The nuclear magnetic resonance study also indicated motion about the C-O axis.

The thermal expansion co-efficients for selenourea are within the range common for small hydrogen bonded molecules (ice, urea, for example). However the interpretation here is complicated by the existence of Se...Se van der Waals contacts which are nearly perpendicular to c and which expand by one per cent over the temperature range used. This, coupled with the fact that the normals to the molecular planes are also almost perpendicular to c, results in α_a being somewhat greater than α_c, and comparison of interatomic distances at the two temperatures suggest that their relative increase does follow the predicted order: van der Waals contacts, hydrogen bonds, covalent bonds, with insignificant changes in the last. The insensitivity of covalent bond lengths to thermal expansion has been found by all workers in this field, a particularly careful study being that of Lonsdale, Milledge and El Sayed (1966) for anthraquinone, where the structure was determined at five temperatures in the range -170°C to 20.5°C. Sklar, Senko and Post (1961) showed that the same was also true of urea, and that the expansion in that case simply resulted in increases in the hydrogen bond lengths.

Refractive index of selenourea.

Bunn (1945) points out that the anisotropic form of index of refraction can be related to crystal structure in the following way. For chain molecules the highest index will be along the chain direction, and for planar molecules, the present case, the lowest refractive index will be perpendicular to the molecular plane. Knowing the structure of selenourea this would predict $n_c > n_a$. This is in fact the case, for the necessary measurements have been performed by Kondrashev and Andreeva, who simply quote the indices as larger and smaller, $n_g=1.84$, $n_p=1.79$. However their calculated value of the molar refractivity identifies these as $n_c=n_g$, $n_a=n_p$, since $\bar{n}=(n_c n_a^2)^{1/3}$ for trigonal crystals.

Conclusion.

The crystal structure of selenourea contains nine independent but identical molecules, the geometry of which is consistent with the analogues urea and thiourea, and with the substituted selenoureas so far studied. The structure confirms the existence of N-H...Se hydrogen bonds. It also suggests that in the urea series a three-fold spiral chain is a particularly stable configuration. However, perhaps the most intriguing problem to the crystal chemist - the rationale behind the large number of non-equivalent molecules - has also proved to have perhaps the most interesting solution. The directional hydrogen bonding and the non-directional van der Waals forces in selenourea reached a complex compromise which sheds light on the competing roles of these effects in molecular crystal structures.

BIBLIOGRAPHY.

Albrecht, G. (1939). Rev. Sci. Instr., 10, 221.

Backer, H.J. and Bos, H. (1943). Rec. trav. chim., 62, 580.

Barnighausen, H., von Volkmann, T. and Jander, J. (1966). Acta Cryst., 21, 571.

Beevers, C.A. and Lipson, H. (1934). Phil. Mag., (7), 17, 855.

Buerger, M.J. (1942). X-ray Crystallography. Wiley, New York.

Buerger, M.J. (1944). The Photography of the Reciprocal Lattice. Am. Soc. X-ray and Electron Diffraction, Monograph No.1.

Buerger, M.J. (1956). Elementary Crystallography. Wiley, New York.

Buerger, M.J. (1959). Vector Space. Wiley, New York.

Buerger, M.J. (1960). Crystal Structure Analysis. Wiley, New York.

Bunn, C.W. (1961). Chemical Crystallography. Oxford University Press, London.

Burbank, R.D. (1951). Acta Cryst., 4, 140.

Burbank, R.D. (1953). Acta Cryst., 6, 55.

Busing, W.R. and Levy, H.A. (1964). Acta Cryst., 17, 142.

Caron, A. and Donohue, J. (1964). Acta Cryst., 17, 544.

Cromer, D.T. and Herrington, K.D. (1955). J. Amer. Chem. Soc., 77, 4708.

Cruickshank, D.J.W. (1949). Acta Cryst., 2, 65.

Cruickshank, D.J.W. (1956). Acta Cryst., 9, 754.

Cruickshank, D.J.W. (1960). Acta Cryst., 13, 774.

Cruickshank, D.J.W. and McDonald, W.S. (1967). Acta Cryst., 23, 9.

Diamant, H., Drenck, K. and Pepinsky, R. (1957). Rev. Sci. Instr., 28, 30.

Dias, H.W. and Truter, M.R. (1964). Acta Cryst., 17, 937.

Dvoryankin, V.F. and Ruchkin, E.D. (1962). Zhur. Strukt. Khim., 3, 342.

Dvoryankin, V.F. and Vainshtein, B.K. (1958). Kristallographija, 3, 559.

Dvoryankin, V.F. and Vainshtein, B.K. (1961). Kristallographija, 6, 949.

Freeman, A.J. and Watson, R.E. (1961). Unpublished work.

Geller, S. and Booth, D.P. (1959). Z. Kristallogr., 111, 117.

Geller, S. and Katz, H. (1962). Bell Syst. Tech. J., 41, 425.

Gilbert, R.E. (1955). Ph.D. Thesis, University of London.

Gilbert, R.E. and Lonsdale, K. (1956). Acta Cryst., 9, 697.

Goldsmith, G.J. and White, J.C. (1959). J.Chem. Phys., 31, 1175.

Grenville-Wells, H.J. (1956). Acta Cryst., 9, 709.

Hamilton, W.C. (1965). Acta Cryst., 18, 866.

Hendricks, S.B. (1928). J. Amer. Chem. Soc., 50, 2455.

Hoerni, J.A. and Ibers, J.A. (1951). Acta Cryst., 7, 744.

Hope, H. (1964). Acta Chem. Scand., 18, 1800.

Hope, H. (1965). Acta Cryst., 18, 259.

Hughes, E.W. (1941). J. Amer. Chem. Soc., 63, 1737.

Iitaka, Y. (1958). Acta Cryst., 11, 225.

International Tables for X-ray Crystallography. See Lonsdale, K.

Ketelaar, J.A.A., Hart, W.H., Moerel, D. and Polder, D. (1939). Z. Kristallogr., 101, 396.

Kitaigorodskii, A.I. (1961). Organic Chemical Crystallography, Consultants Bureau, New York.

Kitaigorodskii, A.I. (1965). Acta Cryst., 18, 585.

Kondrashev, Yu.D. and Andreeva, N.A. (1963). Zhur. Strukt. Khim., 4, 454.

Krackov, M.H., Lee, C.M. and Mautner, H.G. (1965). J. Amer. Chem. Soc., 87, 892.

Krebs, von B. and Gattow, G. (1965). Z. anorg. allg. Chem.,340, 294.

Kumler, W.D. and Fohlen, G.M. (1942). J. Amer. Chem. Soc., 64, 1944.

Kunchur, N.R. and Truter, M.R. (1958). J. Chem. Soc., p.2551.

Lenné, H.U. (1954). Acta Cryst., 7, 1.

Lingafelter, E.C., Orioli, P.L., Schein, B.J.B. and Stewart, J.M. (1966). Acta Cryst., 20, 451.

Lipson, H. and Cochran, W. (1967). The Determination of Crystal Structures. Bell, London.

Lobachev, A.N. and Vainshtein, B.K. (1961). Kristallografija, 6, 395.

Lonsdale, K. (1959). Z. Kristallogr., 112, 188.

Lonsdale, K. (Ed.) (1962). International Tables for X-ray Crystallography. Kynoch Press, Birmingham.

Lonsdale, K. and El Sayed, K. (1965). Acta Cryst., 19, 487.

Lonsdale, K., Milledge, H.J. and El Sayed, K. (1966). Acta Cryst., 20, 1.

Lopez-Castro, A. (1965). Private communication.

Mackay, A.L. (1953). Acta Cryst., 6, 214.

Marsh, R.E. (1952). Acta Cryst., 5, 458.

Marsh, R.E., Pauling, L. and McCullough, J.D. (1953). Acta Cryst., 6, 71.

Mautner, H.G. (1956). J. Amer. Chem. Soc., 78, 5292.

Mikhailov, G.M., Lundin, A.G., Gabuda, S.P. and Aleksandrov, K.S. (1961). Dokl. Akad. Nauk S.S.S.R., 141, 1406.

Mima, K. (1959). J. Pharm. Soc. Japan, 77, 1196.

Nordman, C.E., Patterson, A.L., Weldon, A.S. and Supper, C.E. (1955). Rev. Sci. Instr., 26, 690.

Pauling, L. (1960). The Nature of the Chemical Bond. Cornell University Press, New York.

Perez Rodriguez, M., Cubero, M. and Lopez-Castro,A. (1964). Nature, 201, 180.

Ramsay, I.W. and Rogers, D. (1952). Acta Cryst., 5, 268.

Robertson, B.E. (1966). M.Sc. Thesis. McMaster University.

Robertson, J.M. (1943). J. Sci. Instr., 20, 175.

Rollett, J.S.(1964). Article in Rollett, J.S.(Ed). Computing Methods in Crystallography. Pergamon Press, Oxford.

Sakurai, K. (1958). Acta Cryst., 11, 840.

Sakurai, T. (1965). Acta Cryst., 19, 320.

Scheringer, C. (1965). Acta Cryst., 19, 504.

Shefter, E., James, M.N.G. and Mautner, H.G. (1966). J. Pharm.

Sci., 55, 643.

Shefter, E. and Mautner, H.G. (1967). J. Amer. Chem. Soc., 89, 1249.

Sklar, N., Senko, M.E. and Post, B. (1961). Acta Cryst., 14, 716.

Smith, A.E. (1952). Acta Cryst., 5, 224.

Solomon, A.L. (1956). Phys. Rev., 104, 1191.

Stephens, J.S. (1967). Ph.D. Thesis. McMaster University.

Sutton, L.E. (Ed.) (1959). Tables of Interatomic Distances and Configuration in Molecules and Ions. Special Publication No.11. The Chemical Society, London.

Truter, M.R. (1967). Acta Cryst., 22, 556.

Tsernoglou, D. (1966). Ph.D. Thesis. Yale University.

Verneuil, A. (1886). Ann. Chim., (6), 9, 292.

Waser, J. (1955). Acta Cryst., 8, 595.

Weissenberg, K. (1924). Z. Physik, 23, 229.

Wooster, W.A. (1964). Article in Ramachandran, G.N. (Ed.). Advanced Methods of Crystallography. Academic Press, London.

Worsham, J.E., Levy, H.A. and Peterson, S.W. (1957). Acta Cryst., 10, 319.

Wyckoff, R.W.G. and Corey, R.B. (1932). Z. Kristallogr., 81, 386.

Zvonkova, Z.V., Krivnov, V.Ya., and Khvatkina, A.N. (1966). Kristallografija, 11, 385.