

AD 669749

AD

STUDIES ON STRUCTURAL RELATIONS
IN CRYSTALLINE
AND VITREOUS COMPOUNDS

FINAL TECHNICAL REPORT

by

PEDER KIERKEGAARD

STIG AXRUP

MATS ISRAELSSON

GUNILLA BARVLING

LARS KIHNBORG

KAIJA EISTRAT

ANN KOPWILLEM

LARS-OVE HAGMAN

BARBRO LINNROS

MADELEINE SELEBORG

March 1968

EUROPEAN RESEARCH OFFICE

UNITED STATES ARMY

DDC
RECEIVED
JUN 7 1968
RECEIVED
B

Contract Number DAJA37-67-C-0421

UNIVERSITY OF STOCKHOLM

INSTITUTE OF INORGANIC AND PHYSICAL CHEMISTRY

STOCKHOLM, SWEDEN

Reproduced by the
CLEARINGHOUSE
for Federal Scientific & Technical
Information Springfield Va. 22151

This document has been approved
for public release and sale; its
distribution is unlimited

155

STUDIES ON STRUCTURAL RELATIONS IN CRYSTALLINE
AND VITREOUS COMPOUNDS

FINAL TECHNICAL REPORT

By

PEDER KIERKEGAARD

STIG AXRUP

MATS ISRAELSSON

GUNILLA BARVLING

LARS KIHNBORG

KAIJA EISTRAT

ANN KOPWILLEM

LARS-OVE HAGMAN

BARBRO LINNROS

MADELEINE SELEBORG

March 1968

EUROPEAN RESEARCH OFFICE
UNITED STATES ARMY

Contract number DAJA37-67-C-0421

UNIVERSITY OF STOCKHOLM
INSTITUTE OF INORGANIC AND PHYSICAL CHEMISTRY
STOCKHOLM, SWEDEN

BLANK PAGE

CONTENTS

	Page
ABSTRACT	1
1. INTRODUCTION AND BACKGROUND OF THE RESEARCH	3
2. EXPERIMENTAL METHODS AND DEVELOPMENT WORK	5
2.1. A SIMPLE DEVICE FOR PREPARATION OF AMORPHOUS SUBSTANCES BY VAPOUR DEPOSITION	5
2.2. X-RAY DIFFRACTION TECHNIQUES	5
2.2.1. Phase analysis and crystal structure studies	8
2.2.2. Studies on vitreous materials	8
2.3. MEASUREMENT OF MAGNETIC SUSCEPTIBILITY	10
2.3.1. Description of apparatus and measuring techniques	10
2.4. THERMAL ANALYSIS	18
3. COMPUTATIONAL METHODS EMPLOYED IN X-RAY DIFFRACTION STUDIES	19
3.1. COMPUTER PROGRAMS FOR CRYSTAL STRUCTURE STUDIES	19
3.2. TREATMENT OF X-RAY DIFFRACTION DATA FROM VITREOUS MATERIALS	22
3.2.1. Mathematical background of the computer program ...	22
3.2.2. Functioning of the program	25
3.3. RADIAL DISTRIBUTION FUNCTIONS FOR CRYSTALLINE MATERIALS ..	27
4. RESULTS AND INTERPRETATIONS OF MATERIALS STUDIES	28
4.1. STUDIES ON VITREOUS AND CRYSTALLINE MATERIALS OF COMPO- SITIONS $\text{Na}_2\text{O} \cdot n\text{MO}_3$ ($\underline{M} = \text{Mo or W}$)	28
4.1.1. Preparative work including studies on glass forma- tion and devitrification	28
4.1.2. X-ray diffraction studies	34
4.2. STUDIES ON AMORPHOUS MOLYBDENUM TRIOXIDE	45
4.2.1. Preparative work	45
4.2.2. Properties and recrystallization of the amorphous material	45
4.3. STUDIES ON THE SYSTEMS $\underline{A}_2\text{WO}_4\text{-WO}_3$ ($\underline{A} = \text{K or Rb}$)	47
4.3.1. Studies on the system $\text{K}_2\text{WO}_4\text{-WO}_3$	47
4.3.2. The crystal structure of dipotassium tetra- wolframate	48

	Page
a. Experimental	49
b. Derivation of the structure	49
c. Description and discussion of the structure	56
4.3.3. Studies on the system $Rb_2WO_4-WO_3$	59
4.4. GLASSES AND CRYSTALLINE MATERIALS ON ARSENATE MOLYBDATE (WOLFRAMATE) BASIS	60
4.4.1. Preparative work	61
4.5. STUDIES ON PHOSPHATES OF ZIRCONIUM AND URANIUM	62
4.5.1. The structure of $NaZr_2(PO_4)_3$	63
4.5.2. The structure of $U(PO_3)_4$	63
a. Experimental	63
b. Investigation of the structure	66
4.6. STUDIES ON TERNARY OXIDE SYSTEMS CONTAINING VANADIUM AND MOLYBDENUM OR WOLFRAM	68
4.6.1. The molybdenum vanadium oxide system	69
4.6.2. The wolfram vanadium oxide system	74
4.7. STUDIES ON COPPER WOLFRAM OXIDES	76
4.8. MAGNETIC PROPERTIES ON MOLYBDENUM AND WOLFRAM OXIDE PHOSPHATES	79
5. SOME GENERAL ASPECTS AND PLANS FOR FURTHER RESEARCH	81
ACKNOWLEDGEMENTS	82
REFERENCES	83
APPENDICES:	
I. Tunnel Structure of $K_2W_4O_{13}$	I:1-4
II. Derivation of the Radial Distribution Function for Crystalline Materials from X-Ray Powder Data	II:1-7
III. The Crystal Structure of $(Mo_{0.3}V_{0.7})_2O_5$ of $R-Nb_2O_5$ Type and a Comparison with the structures of V_2O_5 and V_2MoO_8	III:1-16
IV. The Crystal Structure of $NaMe^{IV}_2(PO_4)_3$, $Me^{IV} = Ge, Ti, Zr$	IV:1-20
V. The Crystal Structure of a New Copper Wolfram Oxide Cu_3WO_6	V:1-19

ABSTRACT

The work reported in this document is a continuation of studies on structural relations in crystalline and vitreous compounds containing hexacoordinating and tetraordinating elements.

Studies on the structural properties of crystalline and vitreous polymolybdates and polywolframates have been performed. Results obtained from X-ray studies on sodium dimolybdate and diwolframate are reported and discussed. Details of the structural investigation of dipotassium tetrawolframate are given.

The research work has also comprised some studies on glasses and crystalline substances on arsenate molybdate (wolframate) basis containing alkali or silver atoms.

Structural data are given for the crystalline compounds $\text{NaZr}_2(\text{PO}_4)_3$ and $\text{U}(\text{PO}_3)_4$.

Studies on the structural conditions in the ternary oxide systems containing vanadium and molybdenum or wolfram have been performed. Description of the structures are given for the crystalline phases $(\text{Mo}_{0.93}\text{V}_{0.07})_5\text{O}_{14}$, $\text{W}_{0.375}\text{V}_{0.625}\text{O}_{2.5}$ and $\text{W}_{0.35}\text{O}_{0.65}\text{O}_{2.5}$.

Preliminary results are given for investigations of copper wolfram oxides. X-ray investigations have been performed on the compounds CuWO_{4-x} and Cu_3WO_6 .

The preparation and properties of amorphous molybdenum trioxide are described.

A summary of the types of calculations carried out by computer within this research project is given.

Apparatus and measuring techniques for studies of magnetic susceptibility of vitreous and crystalline specimens have been developed. Measurements over the temperature region $90^\circ\text{K} - 298^\circ\text{K}$ have been performed on the crystalline compounds

MoOPO_4 and $\text{W}_2\text{O}_3(\text{PO}_4)_2$ and glasses prepared from these phases. The crystals of MoOPO_4 have been found to be paramagnetic while the other compounds are diamagnetic.

Plans for further research within this field are outlined.

1. INTRODUCTION AND BACKGROUND OF THE RESEARCH

The research reported in this document has been carried out during the third year of a research program sponsored by the U.S. Department of Army, through its European Research Office. The results obtained during the previous two years have been communicated in two annual reports and also described in a series of published articles and in several papers to be published, viz.:

"Structural Studies on Vitreous Compounds." Contract number DA-91-591-EUC-3635. Final Technical Report (April 1966). (P. Kierkegaard, K. Eistrat, K. Gustafsson, K.-E. Johansson and A. Skancke)

"Studies on Structural Relations in Crystalline and Vitreous Compounds." Contract number DA-91-591-EUC-3980. Final Technical Report (March 1967). (P. Kierkegaard, S. Axrup, B. Linnros, M. Nygren, M. Seleborg, K. Eistrat and M. Sundbäck)

"The Crystal Structure of Dipotassium Trimolybdate." Acta Chem. Scand. 20 (1966) 2195-2201. (M. Seleborg)

"A Refinement of the Crystal Structure of Disodium Dimolybdate." Acta Chem. Scand. 21 (1967) 499-504. (M. Seleborg)

"X-Ray Studies on Some Wolfram Oxide Phosphate Glasses." Arkiv Kemi 27 (1967) 197-212. (A. Skancke and P. Kierkegaard)

"Tunnel Structure of $K_2W_4O_{13}$." Chem. Comm. (1967) 1126-1127. (M. Seleborg)

"The Crystal Structure of $(Mo_{0.3}W_{0.7})_2O_5$ of $R-Nb_2O_5$ Type and a Comparison with the Structures of V_2O_5 and V_2MoO_8 ." Acta Chem. Scand. 21 (1967) 2495-2502. (L. Kihlberg)

"Tracing Phase Transitions by Means of High Frequency ac Measurements Using a Q-meter." Arkiv Kemi 28 (1968) 2217-2221. (M. Nygren and A. Magnéli)

"The Crystal Structure of $NaMe^{IV}_2(PO_4)_3$, $Me^{IV} = Ge, Ti, Zr$." Accepted for publication in Acta Chem. Scand. (L.-O. Hagman and P. Kierkegaard)

"An X-Ray Diffractometer for Investigations of Vitreous and Liquid Materials at Room and Elevated Temperatures." (P. Kierkegaard and K.-E. Johansson)

"Crystal Structure of a New Copper Wolfram Oxide, Cu_3WO_6 ."
(E. Gebert and L. Kihlberg)

"The Crystal Structure of CuWO_{4-x} ." (L. Kihlberg and E. Gebert)

"A Structural Investigation of Uranium(IV) Metaphosphate." (P. Kierkegaard and A. Kopwillem)

Accounts of recent scientific activities have been submitted this year as the following Special and Technical Scientific Reports:

ST & SR No. I: "Tunnel Structure of $\text{K}_2\text{W}_4\text{O}_{13}$."

ST & SR No. II: "Tracing Phase Transitions by Means of High Frequency as Measurements Using a Q-meter."

ST & SR No. III: "The Crystal Structure of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ of $\text{R-Nb}_2\text{O}_5$ Type and a Comparison with the Structures of V_2O_5 and V_2MoO_8 ."

ST & SR No. IV: "The Crystal Structure of $\text{NaMe}_2(\text{PO}_4)_3$, $\text{Me}^{\text{IV}} = \text{Ge}, \text{Ti}, \text{Zr}$."

The reports No. I, III and IV are attached to this document as Appendices.

(N.B.: Report No. II is not included here, as it was presented as Appendix IV of the Annual Report delivered in 1967.)

Additional Appendices attached to the present document include

II. "Derivation of the Radial Distribution Function for Crystalline Materials from X-Ray Powder Data."

V. "The Crystal Structure of a New Copper Wolfram Oxide, Cu_3WO_6 ."

The research has been directed by Peder Kierkegaard, who is also the main author of this report. The members of the group have contributed to the research as indicated in the headings of the various sections of the report.

2. EXPERIMENTAL METHODS AND DEVELOPMENT WORK

In the research reported in this document extensive use has been made of several techniques suitable for the acquisition of information about the constitution of crystalline and vitreous compounds. The methods thus applied have been described in the two previous annual reports (1,2) and, therefore, only some complementary notes are given in this report. The work has, however, also required the application of some other methods which are described below.

2.1. A SIMPLE DEVICE FOR PREPARATION OF AMORPHOUS SUBSTANCES BY VAPOUR DEPOSITION (Lars Kihlberg)

Most vitreous materials investigated within this program have been obtained by quenching from the molten state. An alternative way of preparing amorphous or vitreous substances is by deposition of a vapour on a cool surface. This method is of course restricted to materials which can be heated to give a comparatively high vapour pressure. This is, however, the case for several substances of interest within the present program.

Fig. 1 shows a simple device which has now been successfully applied for the preparation of e.g. molybdenum trioxide in an X-ray amorphous state (cf. sec. 4.2.1). The apparatus consists of an outer glassjacket provided with an outlet to be connected to an evacuating pump via a cold trap. The sample is placed on a platinum strip which can be electrically heated. The deposition of the vapour takes place on the nickel or silver plated closed end of a tube containing the cooling agent (e.g. liquid air). The distance between the sample and the cool^o surface can be varied. The leads to the heating element are introduced through the insulating ring between the jacket and a metal Dewar surrounding the upper part of the cooling agent reservoir.

2.2. X-RAY DIFFRACTION TECHNIQUES

In the research work described in this report X-ray diffraction techniques have been extensively applied. These methods have been applied for investigations of crystalline materials as well as vitreous compounds. Most

Legend to Figure 1

1. Connection to vacuum pump.
2. Brass rods, acting as electrical connection for the strip furnace.
3. O-ring sealings.
4. Connection to cold trap and vacuum pump.
5. Reservoir for cooling agent.
6. Surface where vapour deposition takes place.
7. Electrically heated sample holder made from a platinum strip.
8. Glass tube.

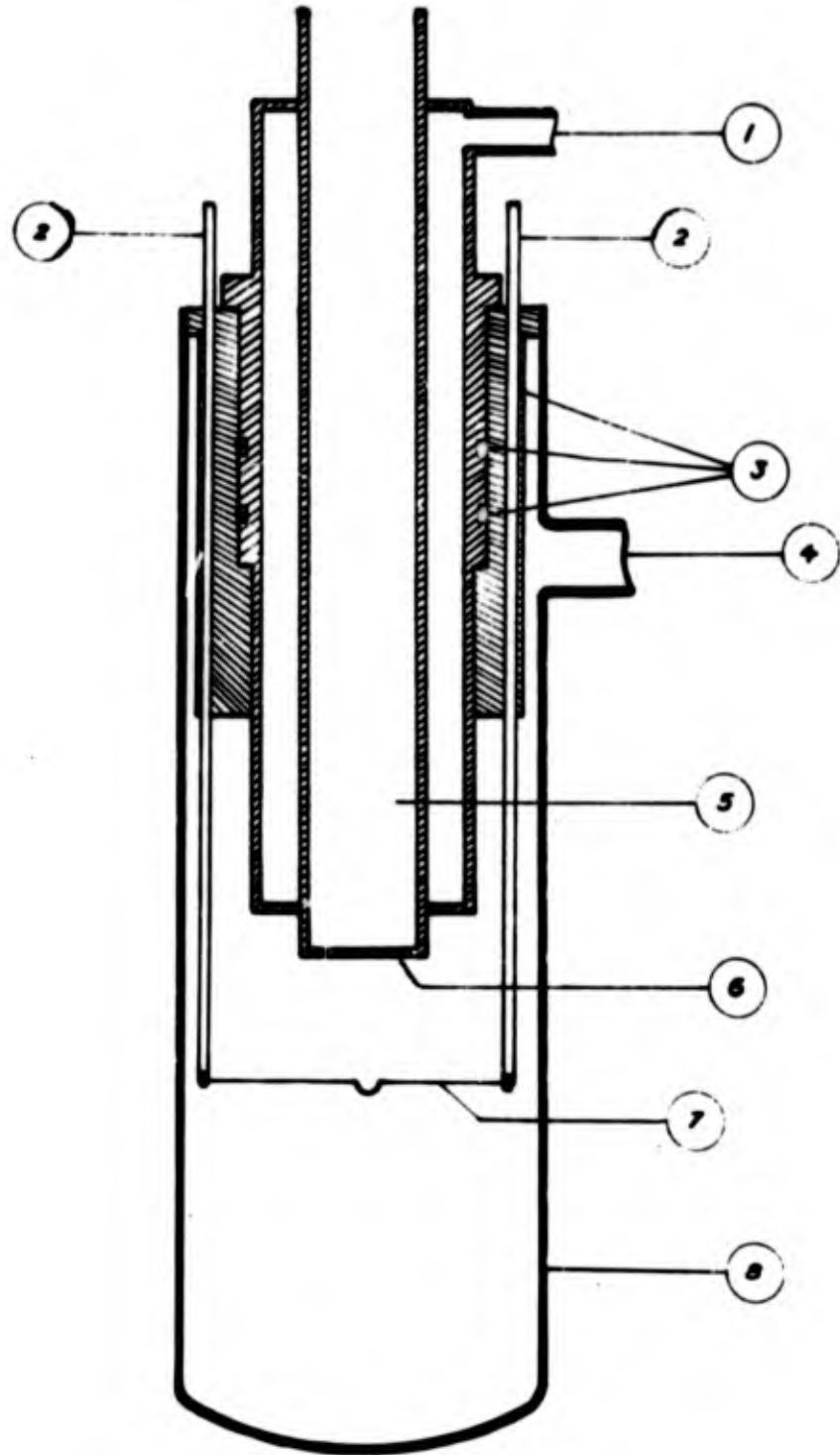


Figure 1. Device for vapour deposition experiments.

of the work has been conducted with well known procedures and commercial or other instrumentation already present at this Institute and also described in the previous annual reports (1,2).

2.2.1. Phase analysis and crystal structure studies

Powder photographs were taken with a Guinier-Hägg focusing camera of 80 mm diameter using quartz (10 $\bar{1}$ 1 plane) crystal monochromatized CuK α ₁ radiation.

Most intensity data from single crystals have been recorded with conventional multiple film technique, on Nonius Weissenberg camera (Cu or Mo radiation). More accurate data have been registered with a scintillation counter on a General Electric SPG Spectrogoniometer equipped with a full-circle single crystal orienter (Goniostat). This arrangement permits investigation of almost the whole of the reciprocal space up to $2\theta \approx 140^\circ$. For a technical description of the instrument, see (3a).

2.2.2. Studies on vitreous materials

The use of a special diffractometer, designed and built at this Institute, for X-ray diffraction studies of vitreous materials has been described in considerable detail in Refs. (1,2). In order to meet the special needs for investigation of melts of alkali isopolywolframates, which have been found to be somewhat aggressive towards the molybdenum and Ni-monic sample holders used so far, another version of this part of the high-temperature X-ray diffractometer has been constructed. In the new version the metal parts are replaced by a ceramic material (alumina). This construction is shown in the schematic drawing Fig. 2.

The scattered intensity from various vitreous materials (cf. sect. 4.1.2) containing molybdenum (Cu radiation) or wolfram (Mo radiation) has been measured using the following experimental conditions:

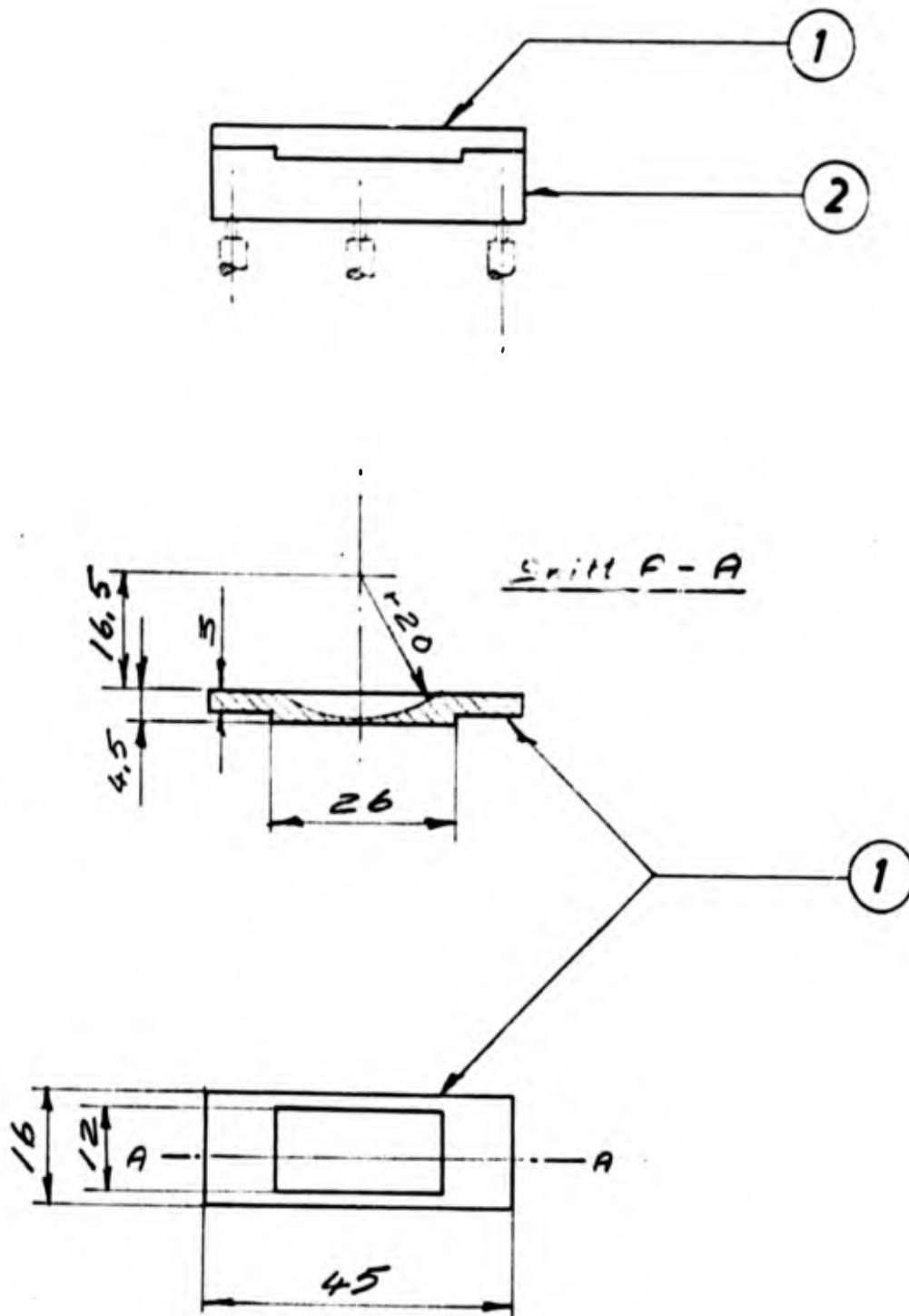


Figure 2. Drawing of the specimen holder.

- 1. Specimen holder made of alumina or platinum.
- 2. Base plate of specimen holder.

	<u>Cu radiation</u>	<u>Mo radiation</u>
Voltage:	40 kV	50 kV
Current:	16 mA	16 mA
Radiation, wavelength:	1.5418 Å	0.7107 Å
Focusing monochromator crystal:	SiO ₂	LiF
Recorded range (θ):	1.75° ≤ θ ≤ 50°	1.75° ≤ θ ≤ 50°
" " (s):	0.25 Å ⁻¹ ≤ s ≤ 6.24 Å ⁻¹	0.54 Å ⁻¹ ≤ s ≤ 13.55 Å ⁻¹
Angular steps (Δθ):	0.25°	0.25°
Number of counts per step:	10.000	10.000

The focusing slit system was adjusted to exclude scattering from the sample holder at low angles. This was accomplished by using a slit opening of 1/12° for $\theta \leq 3^\circ$, 1/4° for $2.75^\circ \leq \theta \leq 10^\circ$ and 1° for $\theta \leq 9.5^\circ$. The resulting intensity curves were normalized in overlap regions.

2.3. MEASUREMENT OF MAGNETIC SUSCEPTIBILITY

The materials studied within this research program on structural relations in crystalline and vitreous compounds containing both hexa-coordinating and tetra-coordinating elements have comprised in the first place molybdenum and wolfram oxide phosphates. The vitreous materials contain metal atoms (molybdenum or wolfram) in an oxidation state less than six (see Refs. 1,2). In order to get more information about the electronic conditions within these materials it was found worthwhile to include measurements of magnetic susceptibility as an auxiliary technique.

2.3.1. Description of apparatus and measuring techniques (Lars Kihlberg)

An apparatus for the measurement of magnetic susceptibility on milligram samples according to the Faraday principle has been constructed. It has been equipped with a cryostat for measurements from liquid air temperature up to room temperature and a furnace covering the range from room temperature up to at least 600°C.

The weight of the sample as well as the force acting on it in the magnetic field is measured by means of a Cahn Gram Electrobalance, Mod. 1570, enclosed in the accessory glass bottle No. 1507. Sample amounts of 4-9 mg and the balance sensitivity range 0-10 mg are normally used. Absolute calibration of the balance is unnecessary since the mass susceptibility is a function of the ratio of the force of the magnetic field and the sample weight. The sample holder used is a platinum micro stirrup-pan (No. 1894) hanging on a quartz fibre. The weight of the empty pan is approximately compensated by counterweights.

The electromagnet is a Varian V-4004 four-inch Laboratory Electromagnet with a V-2300A Power Supply and V-2301A Current Regulator. The pole caps used are V-4084 Tapered Pole Caps the shape of which is indicated in Fig. 3. The pole gap currently used is 43 mm. A field of approximately 8500 gauss of the position of the sample is produced by the maximum magnet current, 4 A.

While the magnet is stationary the balance can be raised to about 35 cm above the normal measuring position in order to facilitate change of sample. This is accomplished by means of a pneumatic elevator with a smooth movement. The measuring level can be adjusted with a stop screw (Fig. 3). The position of the balance (and the sample hanging down from it) in the horizontal plane can also be adjusted relative to the magnet by means of screws.

The cryostat consists principally of three cylindrical shells separated by metal walls surrounding the test tube connected to the balance bottle (Fig. 4). The space between the two outer shells can be evacuated and acts as a metal Dewar. The middle compartment contains the liquid air (or nitrogen), and the innermost one provides possibility to vary the heat flow from the sample. A fine, isolated, copper wire which acts as a heating element is wound around the inner wall, which is also made of copper. When used in the upper temperature range (approximately above 200°K) the space between the two inner shells is evacuated to isolate the sample from the cooling agent as effectively as possible. In order to reach the lowest temperatures one fills it with argon which condenses at liquid air temperatures and gives a high heat transmission. The cryo-

Legend to Figure 3

1. Stop screw.
2. " "
3. " "
4. Tube with balance pan inside the cryostat.
5. Cold trap.
6. Manometer for the elevator pneumatic system.
7. Inlet for compressed gas.
8. To vacuum pump.
9. Inlet for argon gas.
10. Manometer for cryostat.
11. Liquid air level regulator.
12. Inlet for liquid air (or nitrogen).
13. Balance arm.
14. Piston of the pneumatic elevator.
15. Balance supporting arm.
16. Adjustable cryostat support.
17. To vacuum pump (also inlet for nitrogen).

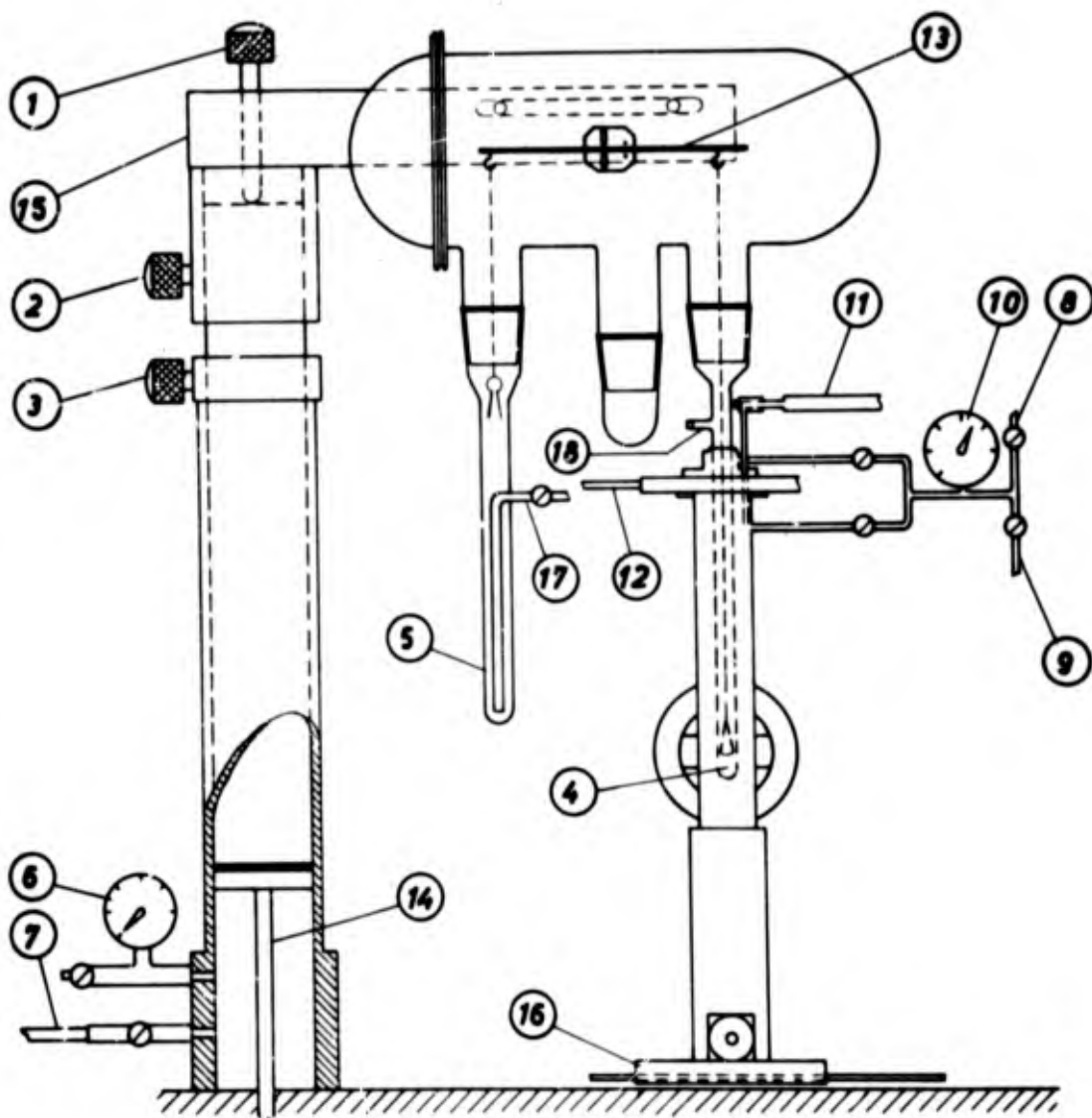


Figure 3. The magnetic susceptibility balance with elevator and the low-temperature attachment mounted on its support.

Legend to Figure 4

1. Inlet for liquid air.
2. To vacuum pump and argon tube.
3. Defrosting element.
4. To vacuum pump.
5. Evacuated space (Dewar vessel).
6. Liquid air reservoir.
7. Inner space.
8. Heating element.

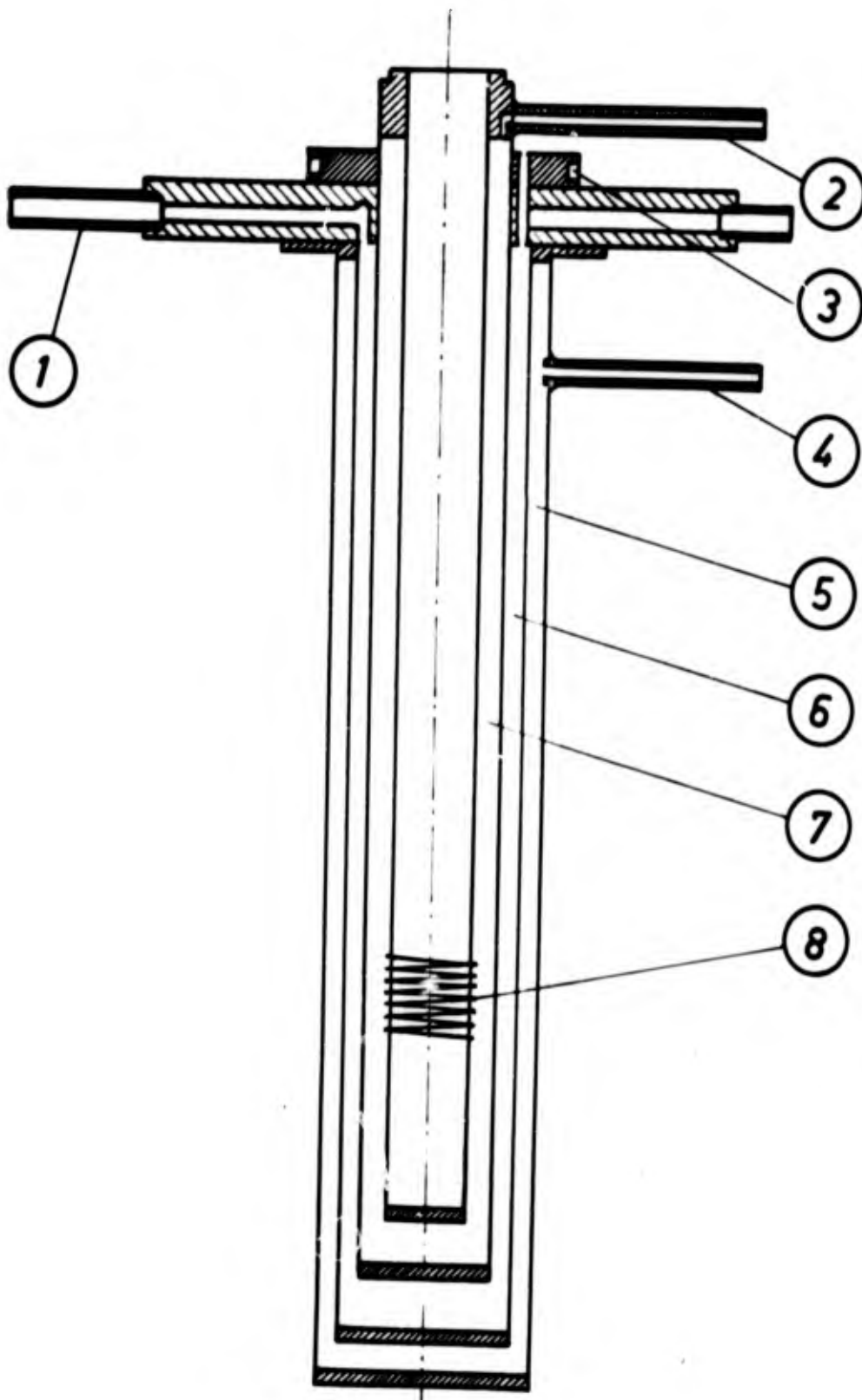


Figure 4. low-temperature attachment to the magnetic susceptibility balance.

Legend to Figure 5

1. Adjustable slit.
2. Slit adjustment screw.
3. Sealing.
4. Inner tube.
5. Outer tube.
6. Connection to vacuum pump.
7. Radiation shield (outer platinum foil).
8. Heating element.
9. Leads to the heating element.
10. Thermocouple.
11. Inner platinum foil.
12. Pole pieces.

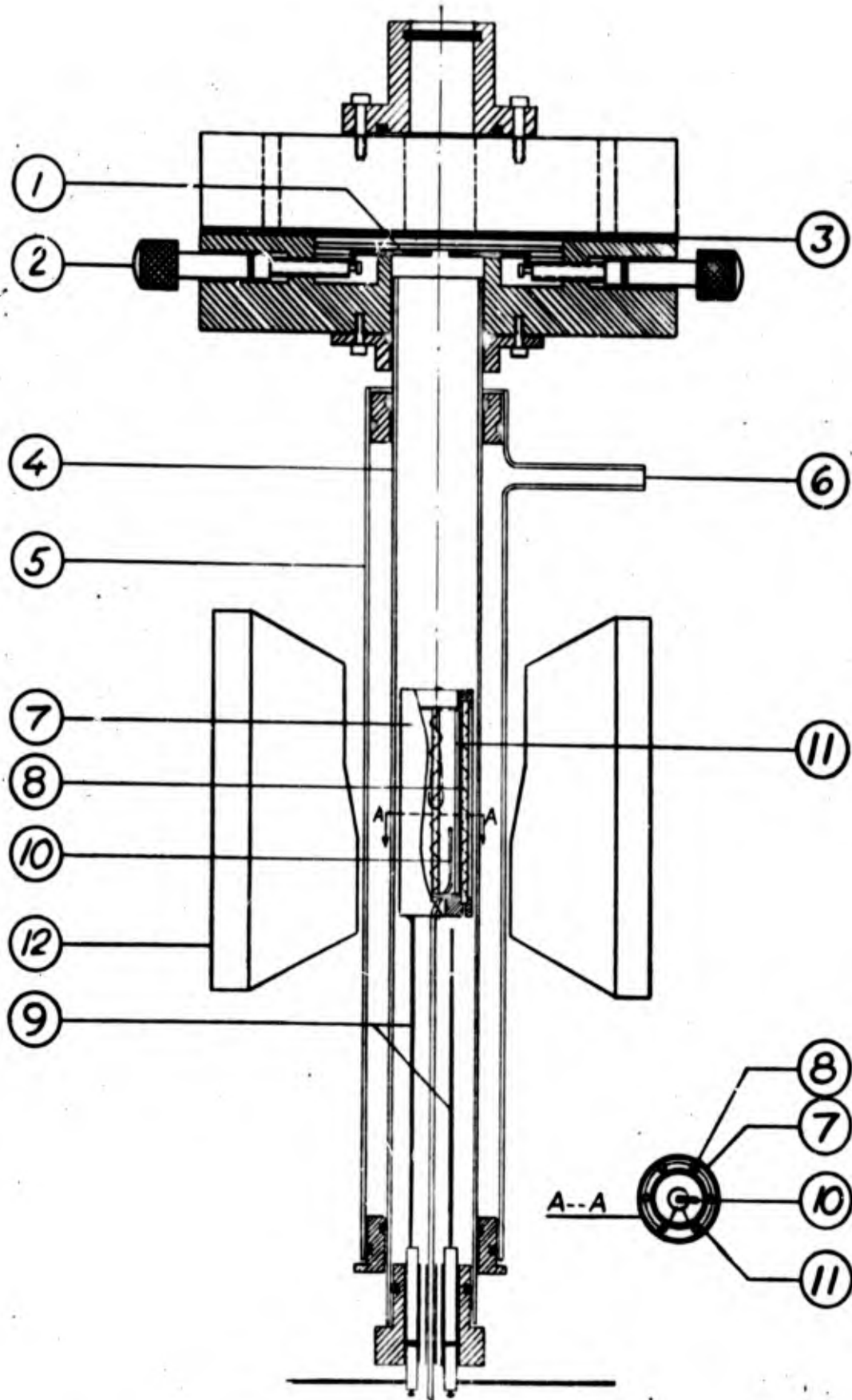


Figure 5. High temperature attachment to the magnetic susceptibility balance.

stat is also equipped with a heating element at the top in order to keep the joints and vacuum sealings there at moderate temperatures. The minimum temperature reached with this cryostat using liquid air as cooling medium is 97°K (measured by means of a copper-constantan thermo-couple inside the test tube and close to the sample position) and with liquid nitrogen 93°K . By variation of the current in the heating element a higher temperature can be arbitrarily selected, which can be held sufficiently constant without the use of any regulator other than an automatic level regulator for the cooling liquid. In order to avoid deposition of ice on the sample or the fibre in the cryostat one removes all moisture from the balance compartment by means of a liquid air cold trap which is applied an hour or so before the cryostat is cooled down.

The furnace (Fig. 5) is at present connected directly to the balance bottle with the test tube removed. The heating element is a platinum wire wound around five vertical ceramic rods, placed outside a cylindrical platinum foil which serves to distribute the temperature evenly over the sample region. It is also surrounded by a cylindrical platinum foil which acts as a radiation shield. Two adjustable slits at the top of the furnace tube are used to reduce the convection streams up into the balance bottle in cases when the system is not evacuated.

All measurements are normally made with several different magnet currents corresponding to values of $H_y \frac{dH_y}{dx}$ within the range $15-50 \cdot 10^5$ gauss²cm⁻¹. The apparatus has been tested and calibrated with $\text{CoHg}(\text{SCN})_4$ and $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

2.4. THERMAL ANALYSIS

In order to obtain a qualitative view of the phase relations at elevated temperatures, melting points, devitrification temperatures etc. differential thermal analyses have been performed. The specimen contained in a platinum crucible was heated in a temperature-controlled electric furnace at a uniform rate ($10^{\circ}/\text{min.}$) and the differential temperature with respect to the standard substance (calcined kaolin) was recorded directly on an xy recorder. The curves thus obtained are given and discussed in the sect. 4.1.1.

3. COMPUTATIONAL METHODS EMPLOYED IN X-RAY DIFFRACTION STUDIES

Extensive use of electronic computers has been one of the most important conditions for the research reported in this document. Some information about the computers and programs used are given below.

3.1. COMPUTER PROGRAMS FOR CRYSTAL STRUCTURE STUDIES

Several programs written or modified by staff members of this Institute (S) and of the Institute of Chemistry, University of Uppsala (U) for the computers mentioned in the list given below, have been employed in these investigations. Some of the programs are included in the second edition of the World List of Crystallographic Computer Programs (3). General descriptions of the programs are available, on request, from the authors.

The following abbreviations are used to indicate:

1800	IBM 1800
3200	Control Data 3200
3600	Control Data 3600

<u>Program</u> (name)	<u>Function</u>	<u>Machine</u>	<u>Author</u>	<u>Ref.</u>
KUSK	Calculates scale factors by comparison of equivalent reflections from different layers	1800	S. Westman (S)	(4)
STYRE	Performs Fourier summations with expanded data stored on tape	1800	R. Karlsson (S)	(4)
SFEXP	Calculates structure factors, expands and stores reflections on tape	1800	R. Karlsson (S)	(4)
TRICLIN	Calculates, for unit cells of general shape, the direct and reciprocal cell parameters	1800	L. Kihlberg (S)	(4)
SFLS	Least-squares, diagonal matrix, refinement of structural parameters	1800	C.-I. Brändén (U) and S. Åsbrink (S) and modified for IBM 1800 by B. Brandt (S) and S. Åsbrink (S)	(3) (4)

<u>Program</u> (name)	<u>Function</u>	<u>Machine</u>	<u>Author</u>	<u>Ref.</u>
STORK STORA STORB STORC DATRE SORTE	This program system stores crystallographic data on disk and/or tape, restores data from disk on tape, corrects cell or reflection data, transforms and reduces indices and reflections, sorts reflection data. The programs are used in combination with subsequent calculations by means of STYRE, SPIS etc.	1800	L.-O. Larsson and L.-O. Hagman (S)	(4)
LAZY	Calculates $\sin^2\theta$ - and d -values with standard deviations from $l(\text{obs})$ and $l(\text{KCl})$ in a Hagg-Guinier camera powder photograph	1800	A. Nord (S)	(4)
ABSW LP EXT	Calculates Lorentz-, polarization, extinction and absorption corrections	1800	P.-E. Werner and M. Leijonmarck (S)	(4)
PIRUM	Program for indexing and determination of accurate cell parameters from powder data by the method of least squares	1800 3600	P.-E. Werner (S)	(4)
DISTAN	Distance and angle calculations with standard deviations	3600	A. Zalkin (Berkeley, Calif.)	(3)
DIST	Distance calculations with standard deviations	1800	A. Zalkin (Berkeley, Calif.) modified by R. Norrestam (S)	(3) (4)
DRF	Data reduction and Fourier programs	3600	A. Zalkin (Berkeley, Calif.) modified by R. Liminga and J.-O. Lundgren (U)	(3)
LALS	Crystallographic least-squares program	3600	A. Zalkin (Berkeley, Calif.) modified by R. Liminga, J.-O. Lundgren and C.-I. Brändén (U)	(3)

<u>Program</u> (name)	<u>Function</u>	<u>Machine</u>	<u>Author</u>	<u>Ref.</u>
DATA CORR	Correction and transformation of crystallographic data stored on magnetic tape	3600	R. Liminga (U)	
DATA P2 EXT DATA	Absorption, Lorentz and polarization and extinction correction of crystallographic data	3600	P. Coppens, L. Leiserowitz and D. Rabinovich (Rehovoth, Israel) modified by O. Olofsson and M. Elfström (U) and by E. Brandt and S. Åsbrink (S)	(3)
GIP	Calculates the setting angles for manual and automatic 4-circle diffractometers	3600 3200	P. Norrestam (S)	(3)
PLANE	Fits a plane to a set of points using the method of least squares	3600	C.-I. Brändén (U)	
ORFLS	Performs least-squares refinement (full matrix) of crystal structure parameters	3600	W.R. Busing, K.O. Martin and H.A. Levy (Oak Ridge, Tenn.) modified by B. Sellberg (U)	(3)
ORFFE	Crystallographic function and error program	3600	W.R. Busing and H.A. Levy (Oak Ridge, Tenn.)	(3)
ORTEP	Program for drawing crystal structure illustrations with a plotter	3600	C.K. Johnson (Oak Ridge, Tenn.)	(3)
SMIN HOMIN	Symmetry and high order minimum function programs	3600	P.G. Simpson, R.D. Dobrott and W.N. Lipscomb (Harvard Univ., Mass.) modified by R. Liminga (U)	(3)

3.2. TREATMENT OF X-RAY DIFFRACTION DATA FROM VITREOUS MATERIALS

In order to obtain radial distribution functions from the experimental intensities of non-crystalline materials (glasses, melts or solutions) registered by means of the special diffractometer (1) the data require extensive computational treatment. These are performed by means of a special program which is described in the following sections.

3.2.1. Mathematical background of the computer program (Stig Axrup)

The data consist of diffracted X-ray intensity measured as a function of diffraction angle. The intensity is a sum of a coherent and an incoherent part, of which the coherent part contains information about the structure of the glass (melt or solution). The intensity function cannot be interpreted in terms of structure by direct inspection, since every measured intensity value contains contributions from all interatomic distances in the glass. In order to make use of the measurements, one has to transform the data so that the number of contributing interatomic distances will be finite and preferably rather small. This end is accomplished by Fourier inversion of the intensity function after the incoherent part has been subtracted. The result is a radial distribution function containing contributions exclusively from the short interatomic distances - up to a chosen maximum distance. The function displays directly the magnitudes of the contributing distances. It also yields an estimate of the number of distances of each magnitude present in the glass structure. Thus, one is furnished with data concerning the coordination around different kinds of atoms in the glass. The coherently diffracted intensity, $I(s)$ from a glass is given by the function:

$$I(s) = \sum_{mn} f_m f_n \frac{\sin(s \cdot R_{mn})}{s \cdot R_{mn}} \quad 1$$

The proof of this equation has been given by several authors (5-7).

The reciprocal vector, \bar{s} , is related to the diffraction angle, θ . Its magnitude is: $s = \frac{4\pi}{\lambda} \cdot \sin \theta$. The atomic scattering factors (which are functions of s) are denoted f_m and f_n for atoms m and n respectively and the distance between those atoms will be called R_{mn} .

For a glass containing several different atoms, $I(s)$ is conveniently expressed in the following manner:

$$I(s) = N \cdot \sum_i f_i^2 + \sum_{mn} \sum_m f_m f_n \frac{\sin(s \cdot R_{mn})}{s \cdot R_{mn}} \quad \underline{2}$$

where a certain formula unit has been selected as a constituent element, and the irradiated sample contains N such elements. The first sum is taken over one formula unit, whereas the second term - the double sum - runs over all different pairs of separate atoms in the entire sample.

A "weighted atomic density function" $\rho_m(r)$, which expresses the average concentration of scattering power at distance r from atom m will be defined in the following manner;

$$4\pi r^2 \rho_m(r) dr = \sum_j f_j \quad \underline{3}$$

where the sum is taken over all atomic centers situated between two concentric spherical shells of radii r and $r+dr$ around atom m . Clearly, the contribution to the diffracted intensity from all interatomic distances of magnitudes r to $r+dr$ between atom m and after atom s is

$$f_m \sum_j f_j \cdot \frac{\sin(s \cdot r)}{s \cdot r} = f_m \cdot 4\pi r^2 \rho_m(r) \cdot \frac{\sin(s \cdot r)}{s \cdot r} dr \quad \underline{4}$$

and expression 2 will take the following appearance:

$$I(s) = N \cdot \left[\sum_i f_i^2 + \sum_m f_m \cdot \int_0^\infty 4\pi r^2 \rho_m(r) \frac{\sin(s \cdot r)}{s \cdot r} dr \right] \quad \underline{5}$$

where both sums, over i and m are taken over the formula unit.

Fourier inversion of $I(s)$ yields the radial atomic distribution function

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \cdot \int_0^\infty s \cdot i(s) \cdot \sin(sr) ds \quad \underline{6}$$

where $i(s) = (I(s) - N \sum_i f_i^2) / N$ and ρ_0 = average atomic density.

In order to use the experimentally determined intensities in expression 6 one must correct them for polarization, absorption and Compton scattering. The relative intensities must then be converted to an absolute scale.

Division of the raw intensities by

$$(1 - \cos^2 2\alpha \cdot \cos^2 2\theta) / (1 + \cos^2 2\alpha) \quad \underline{7}$$

yields polarization corrected intensities, assuming the monochromator, placed in the diffracted beam, to be an "ideally mosaic crystal", which, in turn diffracts the radiation through an angle of 2α (8).

The absorption correction factor A for strongly absorbing samples with a plane surface is (8):

$$A = \frac{1}{\mu} \cdot \frac{\sin(2\theta - \Delta)}{\sin \Delta + \sin(2\theta - \Delta)} \quad \underline{8}$$

where Δ is the angle between sample surface and incident beam direction. For a Bragg-Brentano focusing arrangement ($\Delta = \theta$), expression 8 reduces to:

$$A = \frac{1}{2\mu} \quad \underline{9}$$

since, in this case, A is a constant for all θ it may be included in the scale factor which transforms relative intensities to absolute.

In the following expression:

$$I_{\text{coherent}} = k \cdot I_{\text{corrected}} - I_{\text{incoherent}} \quad \underline{10}$$

I_{coherent} is the $I(s)$ to be used in expression 6, k is a scale factor (including absorption), and $I_{\text{corrected}}$ is the experimental intensity corrected for polarization according to 7. $I_{\text{incoherent}}$ is calculated theoretically and multiplied by a semiempirical factor which takes into account the spectral distribution of the X-rays, losses at the monochromator crystal etc.

The coherent intensity consists of a dominating part deriving from an average atomic density, and, superposed on this, a part con-

taining the structural information. The dominating part of $I(s)$ on the scale of the formula unit is equal to $\sum_j f_j^2$ over the different kinds of atoms in the structure, n_j being the number (not necessarily integral) of atoms with structure factor f_j in the formula unit. The superposed intensity, $\frac{I(s)}{N} - \sum_j f_j^2$, will henceforth be called $i(s)$ (cf. expression 6).

The spurious peaks which are of necessity introduced into the radial distribution function $D(r)$ by the numerical computation of the Fourier integral between finite limits are attenuated and the intensity contributions from different ranges of s are weighted by the introduction of a modification function, $M(s)$, into $D(r)$ which then assumes the following appearance:

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_{s_{\min}}^{s_{\max}} s \cdot i(s) \cdot M(s) \cdot \sin(sr) ds \quad 10$$

The modification function:

$$M(s) = \exp(-bs^2) \cdot sf(s) \quad 11$$

where $sf(s)$ is usually one of the following: 1, $(z_j/f_j(s))^2$ for a particular atom; or $\sum_j z_j^2 / \sum_j f_j^2$ over the different kinds of atoms in the structure.

3.2.2. Functioning of the program (Stig Axrup)

A program written in FORTRAN and intended to be used mainly on an IBM 1800 computer installed at this Institute (cf. 4) has been developed, partly on the basis of an ALGOL program written by Johansson (9).

The input data are:

- 1) A table of θ (degrees) and corresponding I_{obs} values corrected for background
- 2) Atomic scattering factor tables, each entry for any one kind of atom consisting of $\sin \theta/\lambda$, f_0 , $\Delta f'$, $\Delta f''$ and the theoretically calculated value of the atomic contribution to $I_{\text{incoherent}}$
- 3) A table of the semi-empirically found multiplier for $I_{\text{incoherent}}$ as a function of $\sin \theta/\lambda$

For each measured pair of θ and I_{obs} , the program calculates $s = \frac{4\pi}{\lambda} \cdot \sin \theta$ and corrects I_{obs} for polarization.

The total incoherent intensity and the contribution to the coherent intensity from an appropriate average atomic density are calculated for the $\sin \theta / \lambda$ values listed in the scattering factor tables. The values of these functions at the $\sin \theta / \lambda$ values of the intensity measurements are found by interpolation according to Newton's method.

If desired, the result can be pointed out as a table of: θ , I_{obs} (corrected for background), the polarization factor, s , I_{obs} (corrected for polarization), the average atomic density contribution to I_{coherent} , $I_{\text{incoherent}}$ x multiplier and, finally, the sum of the last two quantities.

Scaling of I_{obs} can be effected in two different ways by the program.

The first method is based on the fact that, for large values of s , the total scattered intensity is very nearly equal to the part derived from the average atomic density. Consequently, the I_{obs} values at high θ angles are scaled to match, as nearly as possible the entries on the last column of the table described above. The scale factor thus derived is applied to all I_{obs} values.

The second method for obtaining a scale factor has been originated and described by Norman and Krogh-Moe (9a-9c). The two methods yield very nearly the same result if the intensity has been measured correctly over the whole investigated θ range.

The printed output consists of

- 1) Scale factor
- 2) A table containing: s , $I(s)_{\text{obs}}$ (corrected and scaled), $I(s)_{\text{coherent}}$, $i(s)$ and $s \cdot i(s)$.

If desired, graphs of $I(s)_{\text{obs}}$ (corrected and scaled), and $I(s)_{\text{coherent}}$ can be printed. Furthermore, one has the option of calculating and printing the sum of negative $i(s)$ values and the sum of positive $i(s)$ values. These two sums must have approximately identical absolute magnitudes, which provides a check of the correctness of the calculations.

The Fourier inversion. In the radial distribution function $D(r)$ (expression 10) the integral is approximated by a sum

$$\sum_n^1 [s_n \cdot i(s_n) \cdot M(s_n) \cdot \sin(s_n \cdot r) + s_{n+1} \cdot i(s_{n+1}) \cdot M(s_{n+1}) \cdot \sin(s_{n+1} \cdot r)] \cdot (s_{n+1} - s_n) \quad (12)$$

over the experimental s_n values. There is no facility on the program for calculating a smoothed intensity function. The limits of integration can be chosen arbitrarily by the user of the program.

The printed output consists of a table of r , $D(r)$, $4\pi r^2 \rho_0$, and $D(r) - 4\pi r^2 \rho_0$. Graphs of the three functions are printed simultaneously with the tables.

3.3. RADIAL DISTRIBUTION FUNCTIONS FOR CRYSTALLINE MATERIALS

A direct comparison between the radial distribution functions of vitreous materials and the crystal structure of substances of the same or approximately the same compositions implies some obvious difficulties. The assembly of discrete interatomic distances corresponding to the atomic arrangement of the crystal is not easily compared with the continuous curve of the radial distribution function. An alternative way of comparison is by deriving for the crystalline material a radial distribution function based on the structure factor values corresponding to the crystal structure.

Appendix II presents a procedure for deriving the radial distribution function from X-ray powder data which has been found useful for studies of materials with unknown crystal structures. In the present work a somewhat modified procedure has been applied. The structure factor values corresponding to the known crystal structures are converted to intensities and the radial distribution function is obtained from the expression

$$r[\rho(r) - \rho_0(r)] = K \sum_{i=1}^u \sin \theta_i \quad I(\theta_i) \cdot \sin \frac{4\pi \sin \theta_i}{\lambda} \cdot r \cdot e^{-\left(\frac{\beta \sin^2 \theta_i}{\lambda^2}\right)}$$

4. RESULTS AND INTERPRETATIONS OF MATERIALS STUDIES

4.1. STUDIES ON VITREOUS AND CRYSTALLINE MATERIALS OF COMPOSITIONS $\text{Na}_2\text{O} \cdot n\text{MO}_3$ (\underline{M} = Mo or W)

In the previous annual report on this research project (2) some preliminary results of X-ray diffraction studies on potassium polywolframate glasses after different thermal treatments were described. It was observed that the radial distribution functions derived from the X-ray recordings of such materials showed considerable differences. It was emphasized that any attempt to interpret the findings would require more extensive experimental data.

Part of the work during the present period of research has been conducted with the aim to contribute to the understanding of the observations thus described. In order to simplify as far as possible the interpretation of the radial distribution functions it was found suitable to concentrate the work on studies of sodium polywolframate glasses instead of the potassium compounds. The influence of the relatively heavy potassium atom on the appearance of the distribution function was thus removed. The X-ray scattering power of sodium is practically identical with that of oxygen and the wolfram atoms of the vitreous materials should thus in an admittedly very rough picture be considered as distributed in a "matrix" of light atoms, all having about the same weight.

4.1.1. Preparative Work Including Studies on Glass Formation and Devitrification (Kaija Eistrat)

Investigations of the formation of glasses in the systems $\underline{A}_2\text{O} \cdot n\text{WO}_3$ (\underline{A} = Li, Na, K, Rb and Cs) have been described by Gelsing et al. (10). They report the glass-forming tendency for all the systems mentioned to be highest at compositions around $\underline{A}_2\text{W}_2\text{O}_7$. For the $\text{Na}_2\text{O} \cdot n\text{WO}_3$ system, glasses were obtained within the compositional region $\text{Na}_2\text{O} \cdot 1.5\text{WO}_3$ - $\text{Na}_2\text{O} \cdot 3\text{WO}_3$.

The starting materials for the present preparations were $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ("zur Analyse", Merck), $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (analytical reagent, Mallinckrodt), MoO_3 (analytical reagent, Mallinckrodt) and WO_3 (puriss, KEBO). Na_2WO_4 and Na_2MoO_4 were prepared from the hydrates by melting in a platinum crucible.

Crystalline samples of $\text{Na}_2\text{W}_2\text{O}_7$ and $\text{Na}_2\text{Mo}_2\text{O}_7$ were prepared by the method applied by Seleborg (11), i.e. by melting of stoichiometric mixtures of Na_2MO_4 and MO_3 in a platinum crucible and subsequent heating of the product for about a week at 600°C . Batches of about 20 g of the diwolframate and dimolybdate were thus prepared to serve as starting materials for the preparation of glasses. The X-ray powder patterns registered with $\text{CuK}\alpha_1$ radiation in a Guinier-Hägg type focusing camera were found to be identical with those obtained by Seleborg (11).

Vitreous $\text{Na}_2\text{W}_2\text{O}_7$ was then prepared by melting of the crystalline phase either at 850°C (series I) or 1100°C (series II). The material, which was kept in a platinum crucible, was introduced in furnaces of the above temperatures for one or two minutes, whereupon the melts were rapidly quenched in an ice-water mixture. The vitreous character of the products was checked by visual inspection and by examination with a polarizing microscope and also by the appearance of their Guinier photographs. The weight of the samples did not change appreciably during the treatments. The chemical composition of crystals and glasses should thus be the same.

Using these techniques it was found possible to obtain sodium diwolframate in a vitreous state with batches not exceeding about 0.5 g.

The glasses of series I and II were found to differ slightly in colour. The former, ie. those obtained by melting at 800°C , are colourless while the latter (heating temperature 1100°C) are faintly yellowish.

Portions of the series I and II samples were subjected to further heat-treatment for the subsequent X-ray diffraction work.

This included annealing at 200°C and 300°C for extended periods of time. For these experiments samples of 1.5 g were sealed in evacuated silica capsules. After heating periods of 1, 10 and 30 days respectively, the capsules were rapidly quenched in ice-water mixtures. The products were again studied by visual inspection, with the polarizing microscope and by Guinier photographs. As far as these techniques are concerned the results for the series I and II materials were the same. Thus, the heat-treatment at 200°C did not change the vitreous character or the colour of the material. The samples heated at 300°C were all found to be crystalline. The Guinier photographs differed in intensity with the duration of the heat-treatment, which was interpreted as reflecting the progress of the recrystallization process.

The results thus obtained showed that the vitreous-to-crystal transition of $\text{Na}_2\text{W}_2\text{O}_7$ proceeds fairly rapidly at a temperature between 200°C and 300°C. In order to shed further light on this transition differential thermal analyses were performed for crystalline and vitreous (series I and II) sodium diwolframate. The results thus obtained are represented in Fig. 6. The heating rate was 10°C/min. Both series of vitreous materials show a sharp "exothermic" peak at about 360°C corresponding to a rapid crystallization process. The two thermograms as well as the one yielded by crystalline $\text{Na}_2\text{W}_2\text{O}_7$ show sharp "endothermic" peaks at about 740°C, i.e. the melting temperature. This figure is close to the value 735°C reported by Gelsing et al. (10).

The glass-to-crystal transition temperature of 365°C observed in the DTA studies with a heating rate of 10°C/min. may be compared with the "stability" of $\text{Na}_2\text{W}_2\text{O}_7$ when heated for about a month at 200°C and the transformation of the material within periods of days at 300°C. Preliminary experiments have shown that with much higher rates of heating the transition temperature may be increased to at least 450°C.

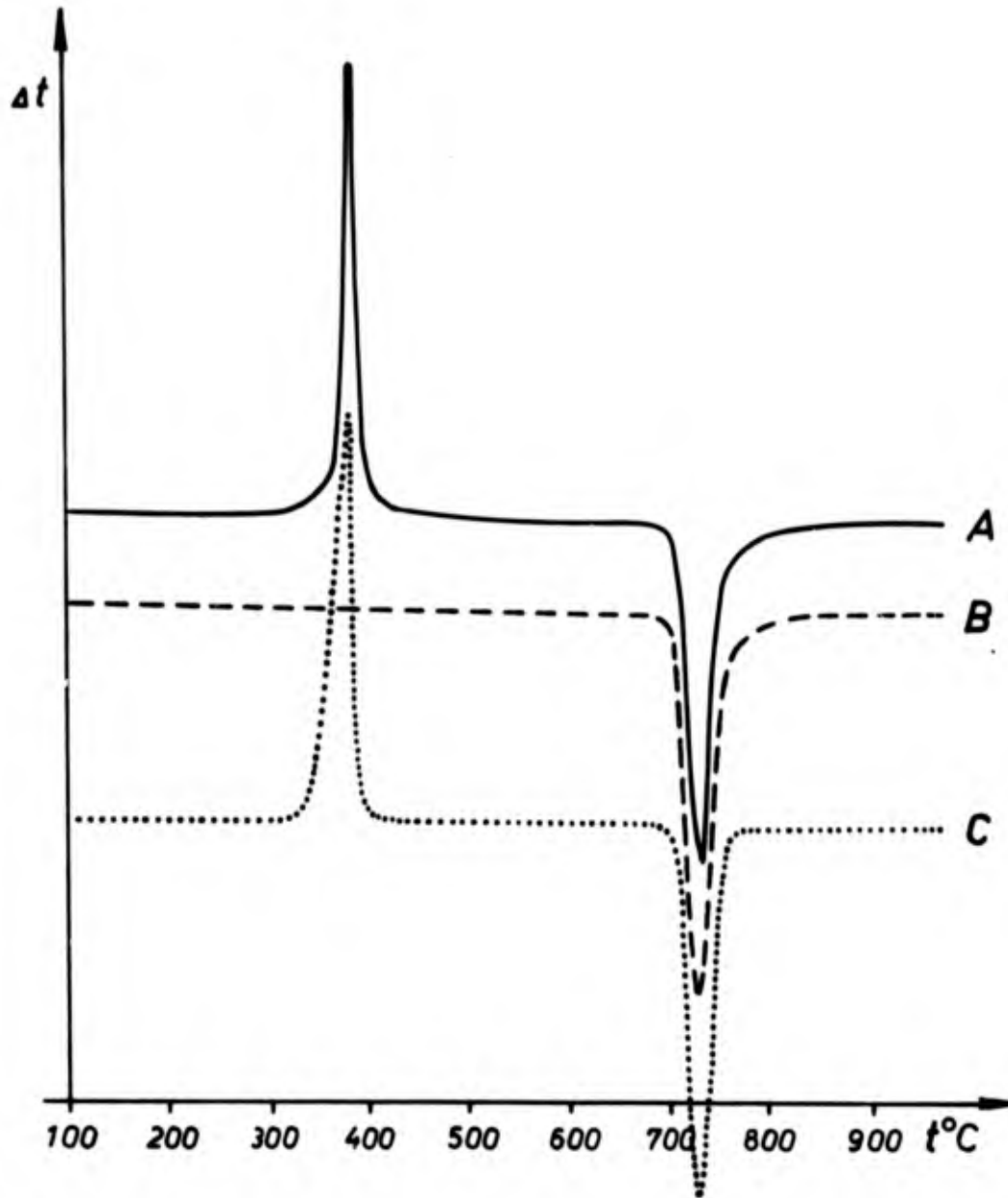


Figure 6. Differential thermal analyses.
Schematic drawing of the curves obtained for $\text{Na}_2\text{W}_2\text{O}_7$.
Glass (I) curve A; crystals curve B and glass II
curve C.

The tendency to glass formation was found to be less with sodium polywolframates higher in WO_3 than was observed with the diwolframate. Thus, applying the techniques described above $Na_2O \cdot 1.5WO_3$ could only be obtained as a glass with batches weighing less than 0.1 g. This amount of $Na_2O \cdot 2.3WO_3$ also resulted in a glassy product. With larger amounts of starting material crystalline products were invariably obtained, obviously due to lower cooling rates. Both of the latter samples have compositions within the "glass-forming" range reported by Gelsing *et al.* (10). The observation made by these authors that $Na_2O \cdot WO_3$ does not form a glass was also confirmed by the present study.

Experiments analogous to those described above with $Na_2W_2O_7$ were also performed for $Na_2Mo_2O_7$. The melting temperature used was $800^\circ C$. With the experimental conditions applied, the amount of the sample could not exceed 75 mg without at least partial formation of crystalline material. The colour of $Na_2Mo_2O_7$ thus prepared was a faintly brownish or yellow one, clearly different from the colourless appearance of the crystalline material.

The synthesis experiments indicated that the glass-to-crystal transition occurs more rapidly with $Na_2Mo_2O_7$ than with $Na_2W_2O_7$. Further studies on this process for $Na_2Mo_2O_7$ were made by DTA analyses. The results thus obtained when heating crystalline and vitreous sodium dimolybdate at a heating rate of $10^\circ C/min$ are represented in Fig. 7. The "endothermic" peak corresponding to the devitrification process between 200° and $300^\circ C$ is not a very sharp one. The melting temperature at $625^\circ C$ is close to the value ($612^\circ C$) reported by Hoermann (12).

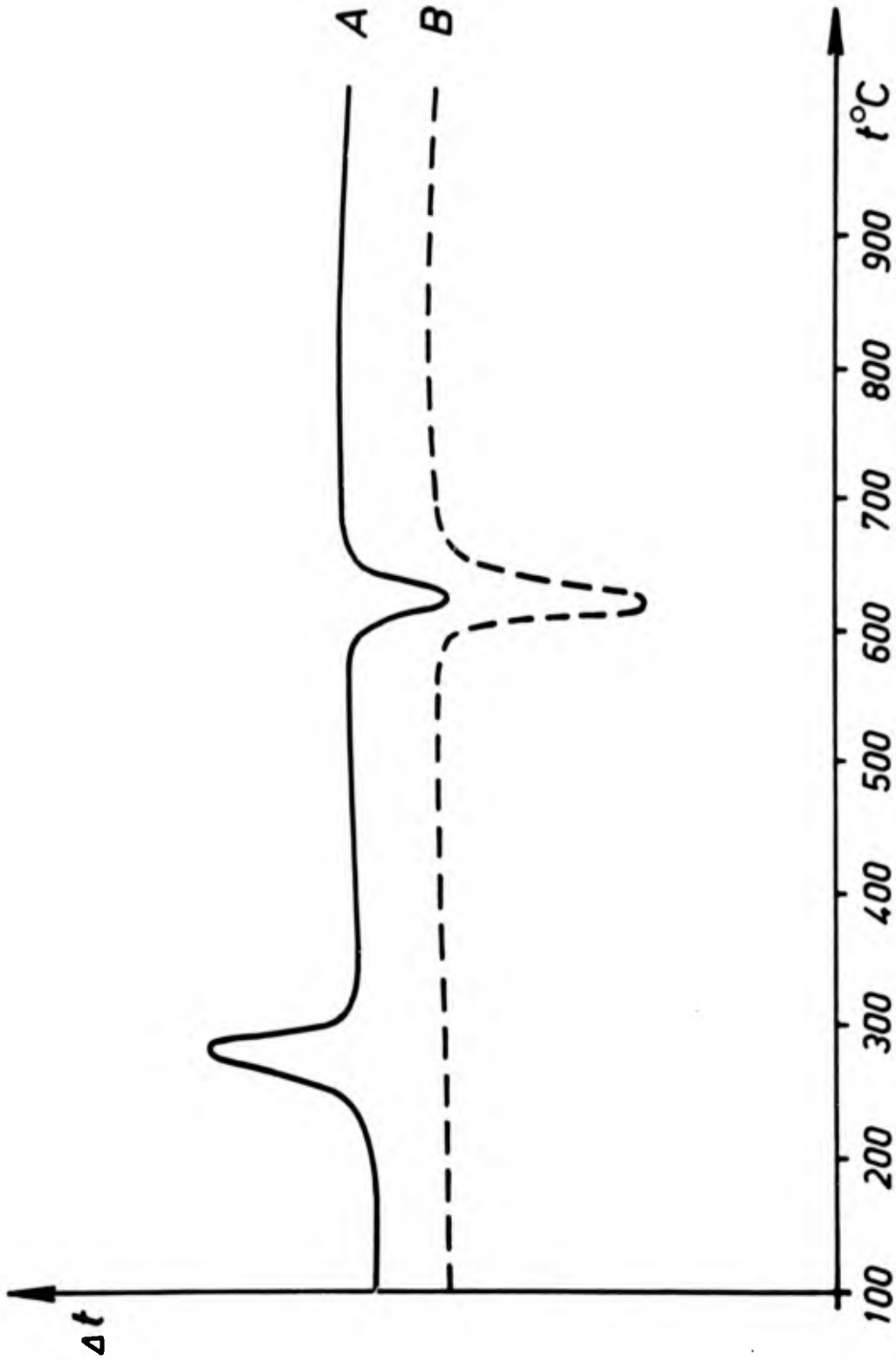


Figure 7. Differential thermal analyses.
Schematic drawing of the curves obtained for
vitreous (A) and crystalline (B) $\text{Na}_2\text{K}_2\text{O}_7$.

4.1.2. X-Ray Diffraction Studies (Barbro Linnros)

The radial distribution function corresponding to the crystal structure of disodium dimolybdate (11,13) and calculated by the procedure described above (sect. 3.3) is illustrated in Fig. 8. This structure contains infinite chains formed by MoO_6 octahedra sharing corners. MoO_4 tetrahedra bridge adjacent MoO_6 octahedra by corner sharing. The shortest Mo-Mo distances of the structure, viz. those corresponding to linking between two octahedra or a tetrahedron and an octahedron are very nearly the same (3.6 Å). The distances between the Mo atoms of octahedra of parallel chains are 5.1 and 7.15 Å. The closest approach between Mo atoms of tetrahedra in a chain is 6.5 Å. Further important interatomic distances of the structure occur around 3.7 Å (Mo-Na distances), 2.8 Å (O-O) and 1.75 Å (Mo-O). (The interatomic distances of $\text{Na}_2\text{Mo}_2\text{O}_7$ are close to those of $\text{Na}_2\text{W}_2\text{O}_7$ which are listed below.) The appearance of the radial distribution function (Fig. 8) is in agreement with the interatomic distances required by the structure. In particular the maxima around 1.9, 2.7, 3.6 and 5.0 Å stand out as corresponding to characteristic groups of interatomic distances of the structure.

Fig. 10 shows the appearance of the radial distribution function for vitreous disodium dimolybdate prepared in the manner described above by quenching from 800°C. The dashed and full curves, which do not differ appreciably, correspond to normalization by the Norman method and by fitting of the intensities at high values of s to a background function based on theoretically calculated scattering amplitudes (cf. Ref. 1, p. 62). The curve of the $\text{Na}_2\text{Mo}_2\text{O}_7$ glass shows considerably less detail than the one given by the crystals. The heavy peak at 3.7 Å, however, stands out very clearly, suggesting that the Mo-Mo distances in the glass are nearly the same as in the crystalline state. The rather flat character of the curve at lower r -values might be due to a less distinct character of the oxygen coordination around molybdenum in the vitreous state. To conclude, however, it may be said that the glass curve shows no indications of other structural elements

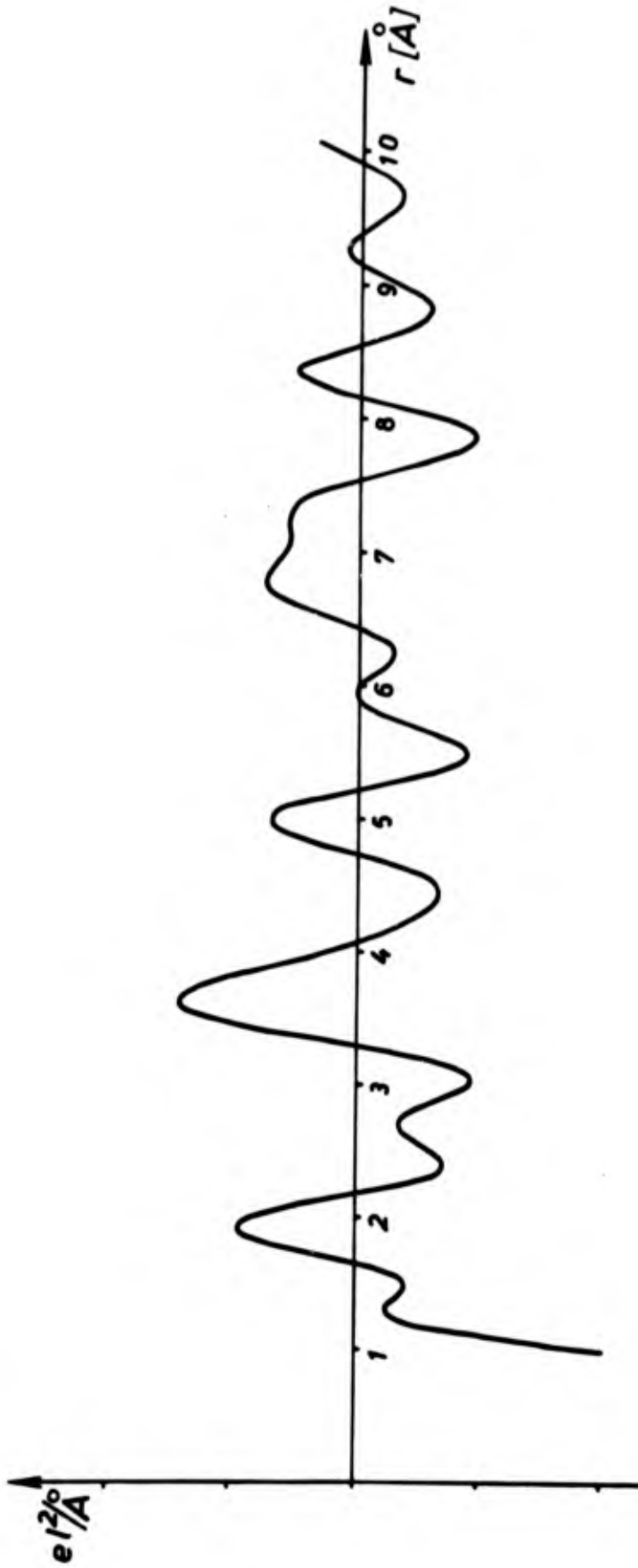


Figure 8. Radial distribution curve for the crystalline compound $\text{Na}_2\text{Mo}_2\text{O}_7$.

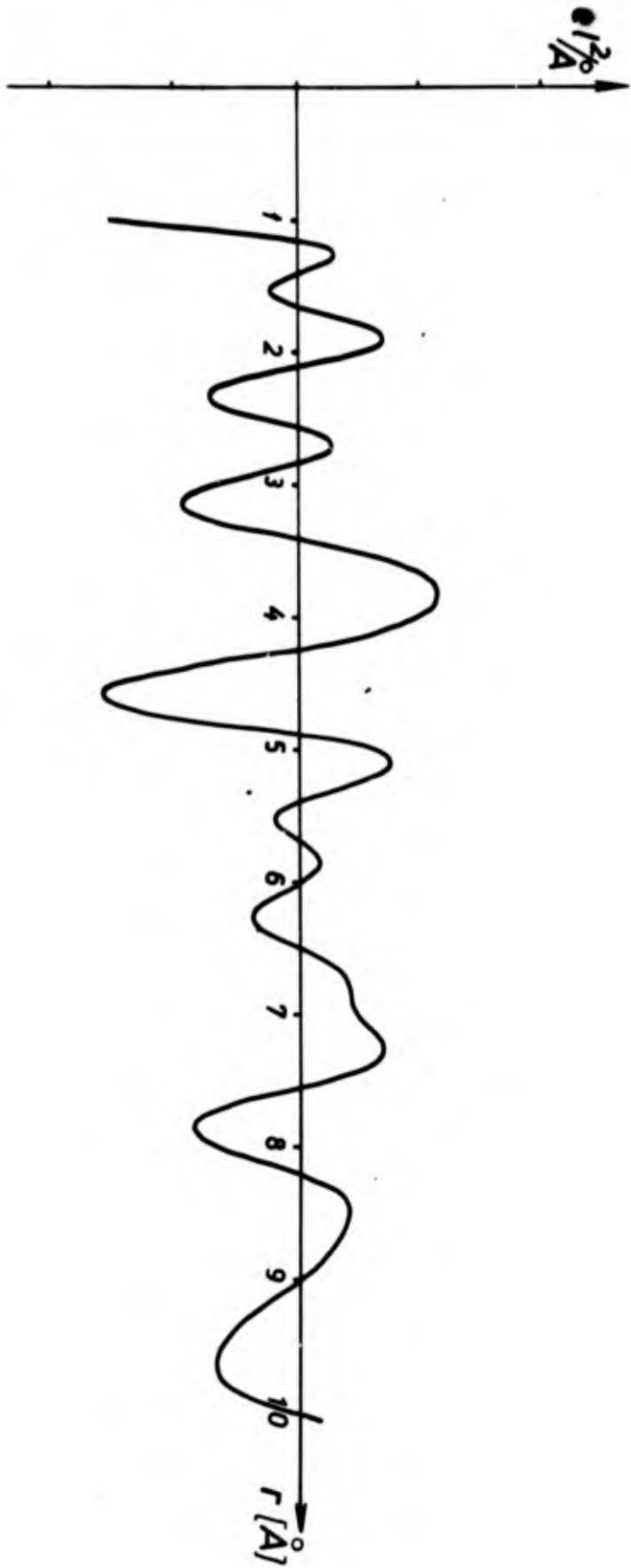


Figure 9. Radial distribution curve for the crystalline compound Na_2WO_7 .

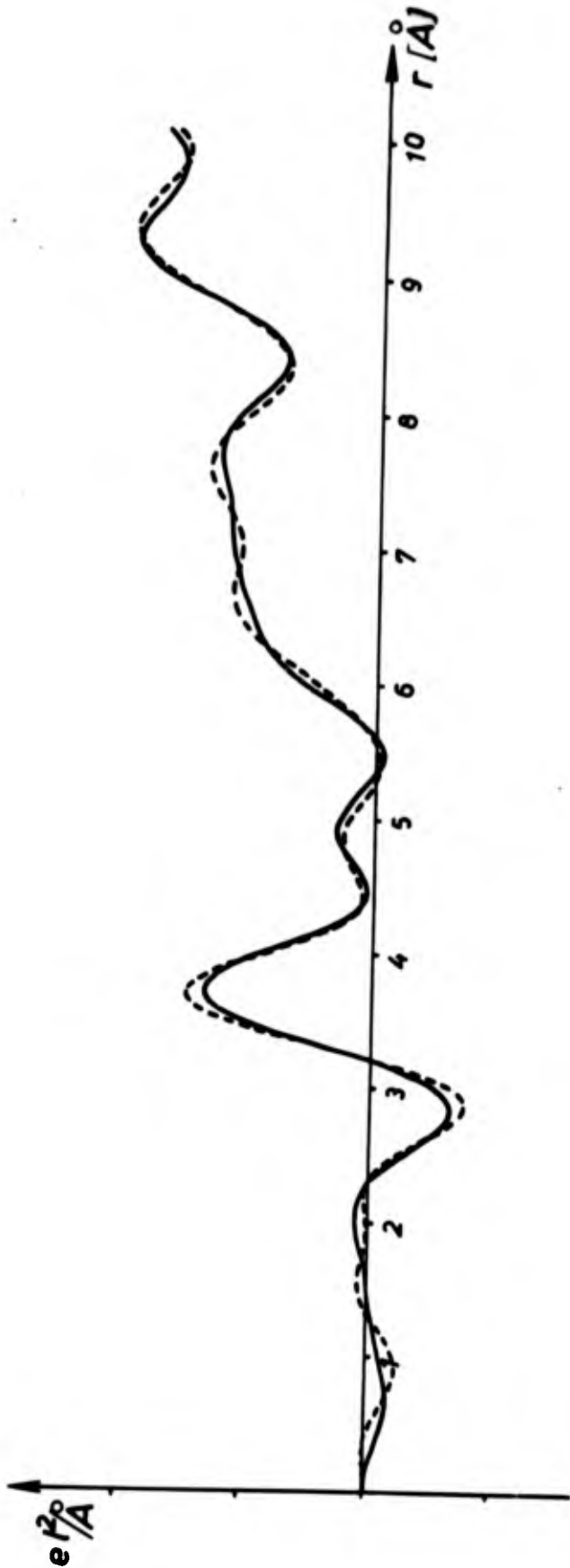


Figure 10. Radial distribution curve for Na₂K_{0.7} glass. The experimental intensity has been normalized by means of the Norman method (dotted curve) or by fitting of intensity values recorded at high values of s to a background function based on theoretically calculated scattering amplitudes (continuous line).

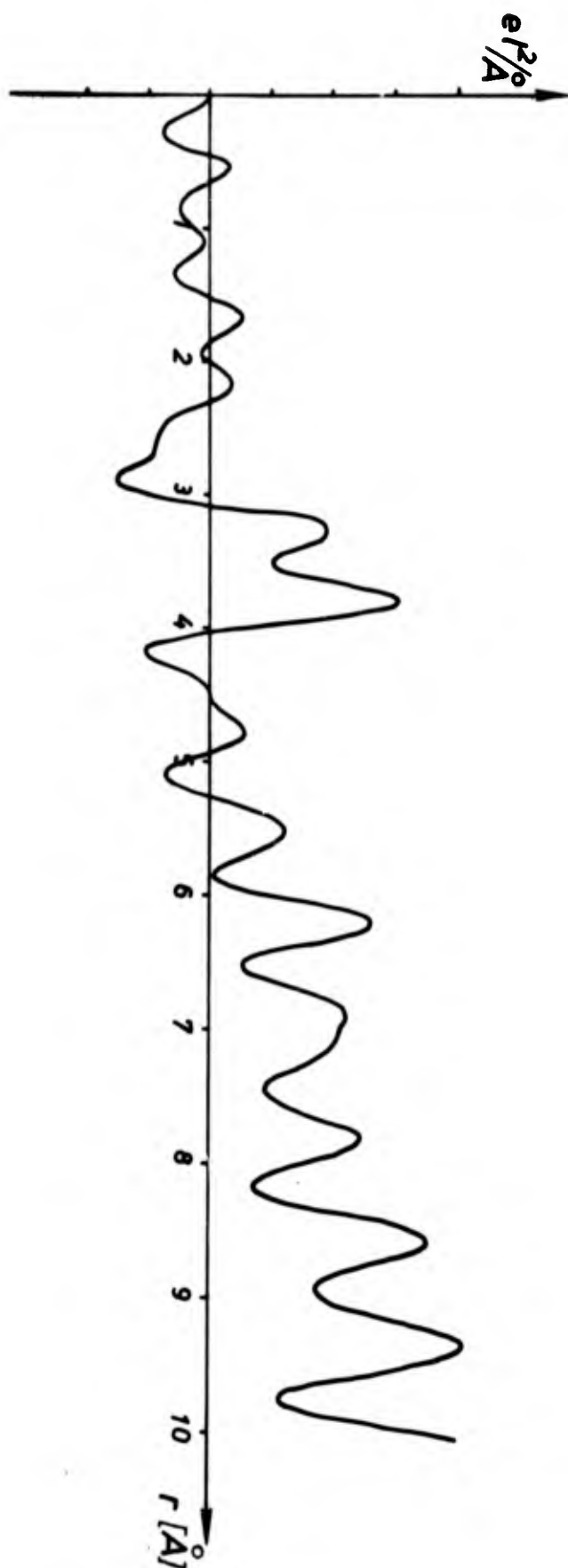


Figure 11. Radial distribution curve for Na_2O_7 -glass.
(Quenched after melting at $800^\circ\text{C}.$)

being present in the vitreous state than in the crystals.

A radial distribution function for crystalline disodium diwolframate is reproduced in Fig. 9. The curve is in satisfactory agreement with the interatomic distances required by the crystal structure (cf. Table 1). The minor differences between the present curve and the one given by crystalline $\text{Na}_2\text{Mo}_2\text{O}_7$ may be attributed to the different scattering powers of molybdenum and wolfram.

Radial distribution functions of vitreous $\text{Na}_2\text{W}_2\text{O}_7$ have been derived on the basis of X-ray diffraction data collected for several samples of different thermal prehistory. Figs. 11-13 reproduce the appearance of some of these curves, viz. those given by the following samples:

$\text{Na}_2\text{W}_2\text{O}_7$ glass, quenched after melting at 800°C (Fig. 11)

$\text{Na}_2\text{W}_2\text{O}_7$ glass, same as preceding one with additional heat-treatment at 200°C for 10 days (Fig. 12)

$\text{Na}_2\text{W}_2\text{O}_7$ glass, quenched after melting at 1100°C and additional heat-treatment at 200°C for 30 days (Fig. 13)

It may be stated that the general character of the three curves is the same. It thus seems rather likely that the three glasses do not show considerable structural differences among themselves. The curve representing the radial distribution function of crystalline $\text{Na}_2\text{W}_2\text{O}_7$ is, on the other hand, rather different in character (Fig. 9). If the comparison is restricted to the r -range 1.5-4 Å, the peaks present in the crystal curve at 1.9 and 2.7 Å may be identified with minor displacements as peaks also appearing in the glass curves. Most striking, however, is the presence of two dominating maxima at 3.25 and 3.75 Å in the latter curves as compared to the single peak at 3.9 Å in the crystal curve. The latter is rather composite in character corresponding not only to W-W but also to W-Na and W-O distances.

The two very sharp maxima present in all the glass curves are most likely to reflect W-W distances. If so, they indicate a marked structural difference to exist in crystalline and vitreous $\text{Na}_2\text{W}_2\text{O}_7$.

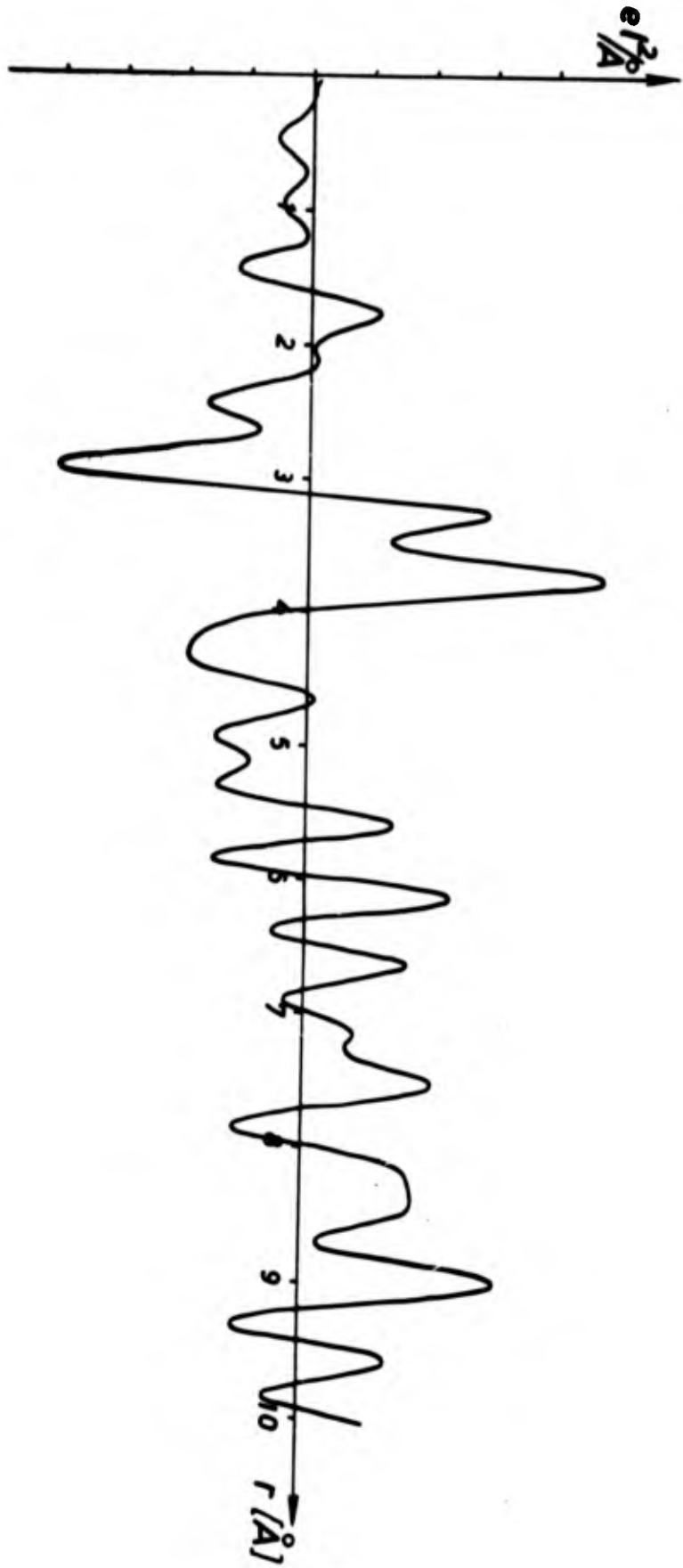


Figure 12. Radial distribution curve for $\text{Na}_2\text{W}_2\text{O}_7$ -glass.
(Quenched after melting at 800°C and heat-treated
at 200°C for 10 days.)

The infinite W_2O_7 chains which are the structural elements of the former state can thus hardly be preserved in the glasses. If W_2O_7 chains, Fig. 14 are to be dismembered into minor species the atomic ratio of oxygen to wolfram of 3.5 requires that the coordination number of oxygen around the metal atom is reduced and/or the number of oxygen atoms common to polyhedra increases over one. In this connection the studies on polywolframate glasses performed by Gelsing et al. (10) by means of infrared measurements are of considerable interest. These authors concluded that the coordination number of wolfram is four in the vitreous state. If this were the case in the diwolframate glasses these would in the simplest case contain $W_2O_7^{2-}$ groups. Assuming normal W-O distances and a W-O-W angle of 130° the W-W distance would be about 3.25 Å, in good agreement with the position of one of the heavy peaks in the radial distribution function. With this model or with more complicated ones implying the presence of aggregates of different sizes, formed by WO_4 tetrahedra linked by corners it seems rather difficult to account for the very sharp maximum at 3.75 Å. The latter is the normal distance for WO_6 octahedra joined by corners and also close to the value for octahedra and tetrahedra linked in this way.

The presence of the two sharp heavy maxima at 3.25 and 3.75 Å might be accounted for by assuming a model consisting exclusively of WO_6 octahedra joined by edges and corners to compact groups of low oxygen to wolfram ratio similar to atomic arrangements found by Lindqvist to be present in e.g. the paramolybdate ion $Mo_7O_{24}^{6-}$ (12b).

It may be said, however, that relatively small groups, be they composed of small numbers of tetrahedra or octahedra, are not very likely to favour the formation of a glass. A vitreous state is often thought to be more easily adopted by substances containing structural units of considerable extensions and likely to be readily distorted. From this point of view it would seem rather likely that $Na_2W_2O_7$ glass does not contain just wolfram-oxygen aggregates of one kind but rather a mixture of groups showing structural characteristics of the various kinds outlined above.

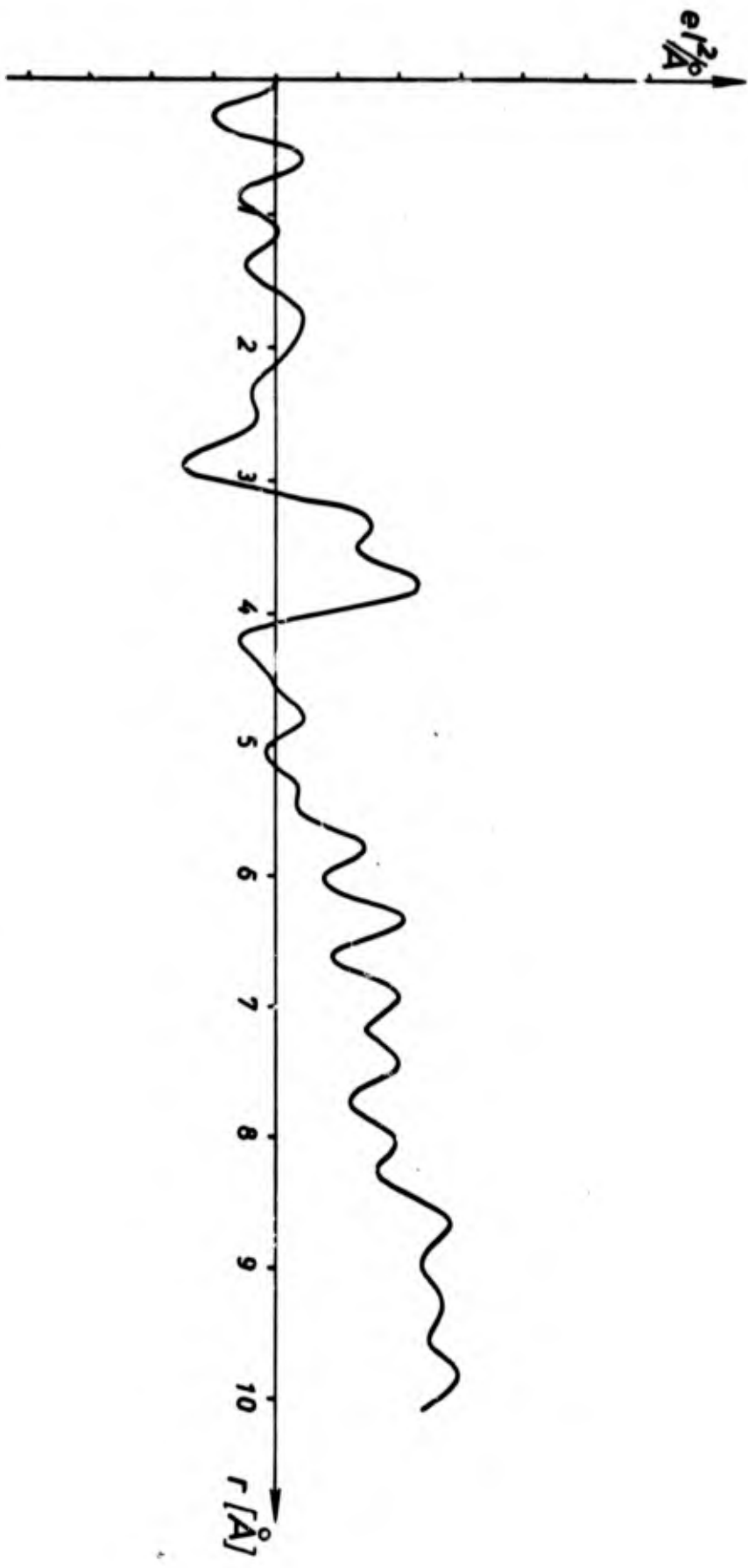


Figure 13. Radial distribution curve for $\text{Na}_2\text{V}_2\text{O}_7$ -glass.
(Quenched after melting at 1100°C and heat-treated
at 200°C for 30 days.)

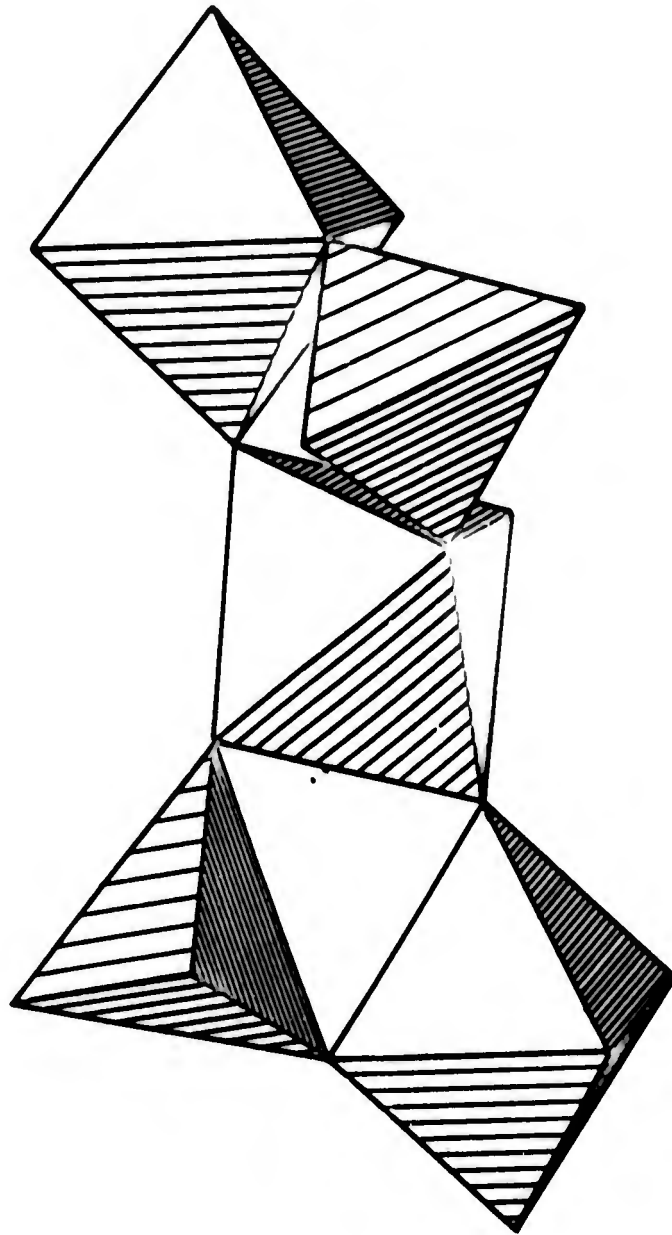


Figure 14. Part of the infinite chain ion $\text{M}_2\text{O}_7^{2-}$ ($\text{M} = \text{Mo}$ or W) of the sodium dimolybdate (diwolframate). Idealized with regular polyhedra. (The figure from Ref. 12b.)

The ideas put forward on the structure of vitreous $\text{Na}_2\text{W}_2\text{O}_7$ are not applicable to the data found for $\text{Na}_2\text{Mo}_2\text{O}_7$ in the glassy state. It has been suggested above that the atomic arrangement of the latter preserves considerable similarities with the one present in crystalline $\text{Na}_2\text{Mo}_2\text{O}_7$. If one considers that the dimolybdate and diwolframate of sodium are isomorphous the marked difference between the structural arrangements in the vitreous state is a rather surprising and interesting result of the research.

Table 1. The most important distances (average values) in the crystal structure of $\text{Na}_2\text{W}_2\text{O}_7$ and their weight factors.

Type of distance	Number of distances	Length in Å
W - W	5	3.58
	3	4.99
	3	5.62
	5	6.09
	4	6.50
	9	7.19
	7	7.60
W - Na	20	3.71
	6	5.21
	16	6.27
W - O	10	1.72
	4	2.26
	9	3.46
	12	4.00
	21	4.43
	17	4.84
	16	5.16
	7	5.43
Na - Na	6	3.60
Na - O	19	2.45
O - O	32	2.76
	11	3.24

4.2. STUDIES ON AMORPHOUS MOLYBDENUM TRIOXIDE (Lars Kihlberg)

The device described above (sect. 2.1) for deposition of metal oxide vapours on a cool surface has been found very useful for the preparation of MoO_3 in an amorphous state. During the course of this work the preparation of amorphous MoO_3 by a different method has been reported by Sarjent and Roy (14). The samples thus obtained, however, also contained crystalline material.

4.2.1. Preparative work

In the present study samples of 10-50 mg of MoO_3 were placed on the platinum strip. The system was evacuated whereupon the element was heated to temperatures roughly in the region 600-900°C for periods of time ranging from 2 to 15 min. The cooling agent was either liquid air or a dry ice-alcohol mixture. The deposit thus obtained on the cool surface could easily be removed after the experiment. Considerable amounts of a very slightly greenish material were thus collected.

4.2.2. Properties and recrystallization of the amorphous material

The character of the deposit was studied by the taking of X-ray photographs and by infrared spectroscopy. The appearance of the X-ray pictures was clearly that of an amorphous material. The IR spectra obtained are represented in Fig. 15, which also gives the corresponding curve for crystalline MoO_3 .

The two curves show very striking differences. Thus, the transmission minimum at 990 cm^{-1} ascribed to a $\text{Mo}=\text{O}$ stretching band and the less sharp minima at lower frequencies characteristic of the crystalline material are absent in the curve of the amorphous substance which shows far less detail within this range of frequency. At higher frequencies, however, amorphous MoO_3 shows transmission minima not given by the crystals, viz. at 1400 and 1600 cm^{-1} and in the 3000-3500 cm^{-1} region. Such minima are encountered in materials containing hydroxide groups and it seems rather likely that in the

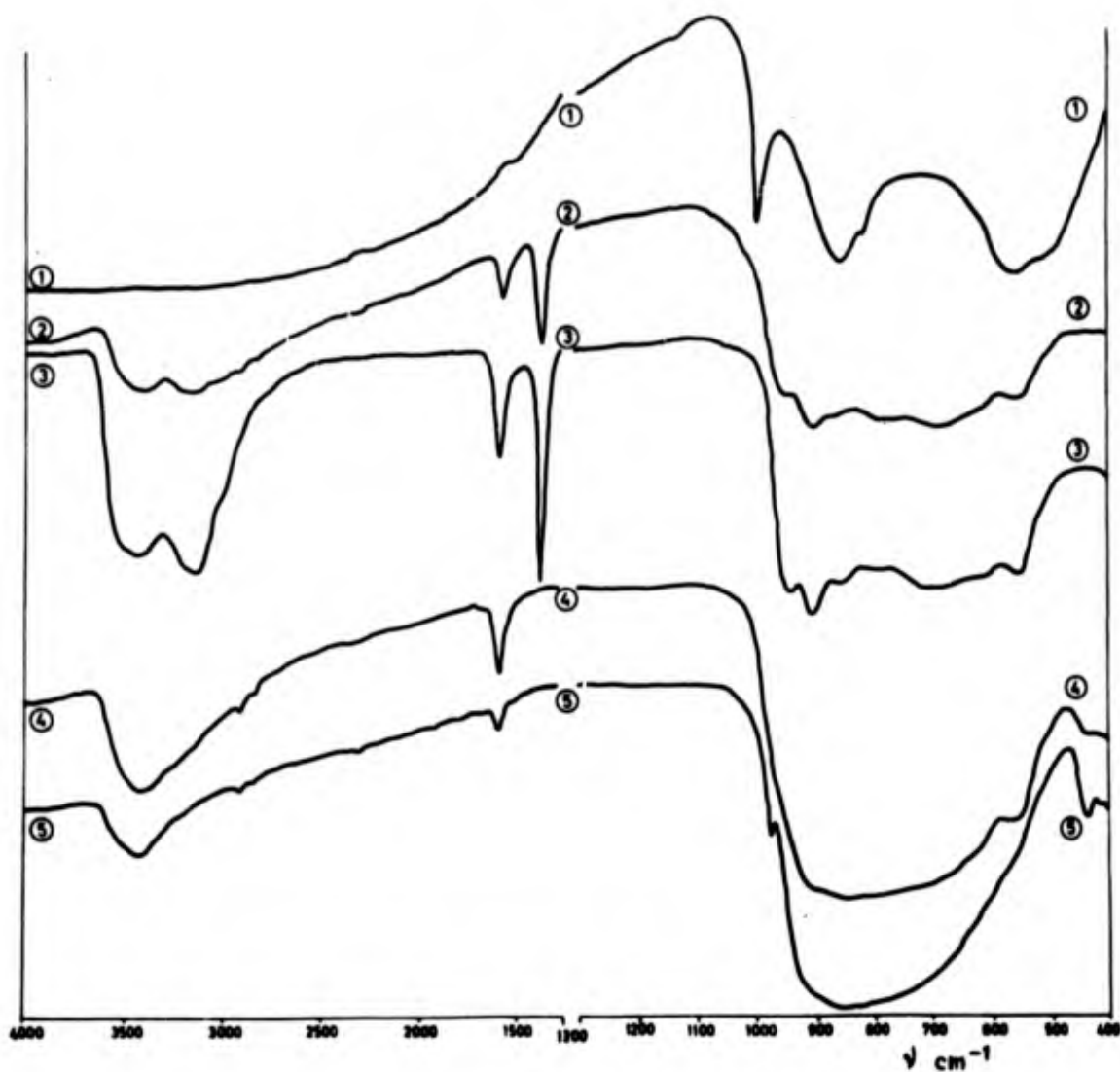


Figure 15. IR spectra of molybdenum trioxide treated in various ways.

1. Original crystalline sample (resublimed).
2. Sample A, obtained by vapour deposition on a surface cooled by liquid air.
3. Sample A after being kept for one day in air.
4. Sample A heated a few seconds in air. Dark blue-green sample.
5. Sample A heated a few minutes in air. Yellow greenish sample.

present case they indicate a hygroscopic character of amorphous MoO_3 not exhibited in the normal crystalline state. This is also supported by the marked increase of the absorption at those frequencies when the sample is exposed to the laboratory atmosphere over night. (Fig. 15, curve 3). Experiments to test this hypothesis are now being made using dry-box techniques in order to prevent any exposure of the amorphous material to moisture. The general idea so far arrived at is that if the interpretation of the observations advanced above holds true the water absorption power of amorphous MoO_3 is a very strong one.

Some preliminary experiments on the recrystallization of amorphous MoO_3 may also be mentioned here. Gradual heating of the samples in air was found to change the colour from almost white to deep blue-green. Upon further heating a gradual change into the normal yellowish white of crystalline MoO_3 was found to take place. The latter product was characterized as crystalline MoO_3 by its X-ray powder pattern. The IR curve of the intermediary materials showed a gradual transition towards the spectrum of the crystalline material. The features in the high frequency range was thus successively disappearing while the 990 cm^{-1} peak which is characteristic for the crystals appeared (Fig. 15 curve 4 and 5).

4.3. STUDIES ON THE SYSTEMS $\underline{\text{A}}_2\text{WO}_4\text{-WO}_3$ ($\underline{\text{A}} = \text{K or Rb}$)

4.3.1. Studies on the system $\text{K}_2\text{WO}_4\text{-WO}_3$

Attempts have previously been made to synthesize $\text{K}_2\text{W}_3\text{O}_{10}$ which, when heated above the melting point (718°C) decomposes into $\text{K}_2\text{W}_4\text{O}_{13}$ and K_2O . By use of a very slow cooling rate it has been possible to obtain the triwolframate.

To the stoichiometric composition $\text{K}_2\text{WO}_4 + 2 \text{WO}_3$ an excess of K_2WO_4 was added to increase the probability of obtaining a product of the desired composition. Mixtures with 0, 1, 5 and 10 (weight) per cent excess K_2WO_4 kept in unsealed silica tubes were heated to 750°C and allowed to cool to 600°C at a rate of 2°C an hour. Guinier powder photographs were taken which showed the pattern of $\text{K}_2\text{W}_3\text{O}_{10}$ as given

by Gelsing et al. (15). The mixture with 10 per cent excess K_2WO_4 gives a phase consisting of yellow needle-shaped crystals contrary to the three other compositions which gave colourless crystals. This phase produced a powder pattern which differs slightly from the others but is in accordance with the powder photograph of $Rb_2W_3O_{10}$ and mixed products such as $K_2Mo_{1.5}W_{1.5}O_{10}$ and $K_2MoW_2O_{10}$.

A preliminary single crystal investigation of the yellow triwolframate has been made. The symmetry is hexagonal as is also the case with $K_2W_4O_{13}$, the structure of which is given in this report. From the Weissenberg photographs it seems probable that there are mirror planes perpendicular to and also parallel to the c axis. The c axis, 3.86 Å, is of the same length as in $K_2W_4O_{13}$ (3.85 Å). It is also interesting to compare the length of the a axes of $K_2W_3O_{10}$ which are about 7.7 Å to the length of the a axes in $K_2W_4O_{13}$ i.e. 15.53 Å. These values make the volume of the unit cell of $K_2W_3O_{10}$ one quarter of the volume of the tetrawolframate cell which contains three formula units. Accordingly, the cell content of the triwolframate would be one formula unit.

Listed d -values calculated from powder photographs have been given by Gelsing (15) and Caillet (16) for the di-, tri-, and tetrawolframates. The two authors give different sets of d values for $K_2W_2O_7$. Furthermore, our values do not agree with either listing. The d values of $K_2W_3O_{10}$, as determined by both authors, are in accordance with our data. In the case of $K_2W_4O_{13}$ the two authors' sets of d -values differ. Our values show agreement with those of Gelsing et al. (15).

4.3.2. The crystal structure of dipotassium tetrawolframate (Madeleine Seleborg)

Investigations of the structures of some alkali isopolymolybdates have previously been carried out at this Institute (11, 17). As the corresponding alkali isopolywolframates should be expected to display analogous crystallographic features it was thought worthwhile to extend the investigations to include some of the phases in

the system $WO_3-A_2WO_4$ where A stands for alkali metal. The system $WO_3-K_2WO_4$ was first studied extensively by Hoermann (12) who established the presence of intermediary phases of the composition $K_2W_3O_{10}$ and $K_2W_4O_{13}$. More recently, this system has been investigated by Gelsing et al. (15) who observed a range of glass formation. Crystal studies of the intermediary phases should therefore prove valuable to elucidate the structural conditions of wolfram in the vitreous state as well.

a. Experimental

Dipotassium tetrawolframate was formed when an intimate mixture of potassium wolframate (British Drug Houses Ltd) and wolfram trioxide ("Baker's Analyzed", J.T. Baker Chemical Co., USA) was heated at $750^\circ C$ in a platinum crucible. The Guinier powder photograph of the product obtained agrees well with the list of d-values given for $K_2W_4O_{13}$ by Gelsing et al. The crystals were of a faintly green colour and had the shape of very long thin needles adhering very strongly to each other, which condition made it difficult to locate a single crystal. The one finally found was of an awkward shape being very long and thin but was, however, mounted in the needle direction for recording of Weissenberg data of the layer lines hk0-hk2. CuK radiation and multiple film technique were used. The intensities of the 434 independent reflections were measured visually by comparison with an intensity scale obtained by photographing a reflection from this crystal with different periods of exposure.

All calculations were performed on a CD 3600 computer. The atomic scattering factors used were those of unionized W, K and O with the real part of the dispersion correction applied to the scattering factors of W and K.

b. Derivation of the structure

The Weissenberg photographs showed hexagonal symmetry. The unit cell dimensions were determined by the method of least squares from a powder pattern recorded in a Guinier focusing camera using CuK₁ radiation and with potassium chloride as an internal standard. The cell parameters thus obtained were a = $15.530 \pm 0.003 \text{ \AA}$ and c = $3.8502 \pm 0.0007 \text{ \AA}$, z = 3.

On account of the strong resemblance in intensity distribution between the $hk0$, $hk1$ and $hk2$ layer lines it was assumed that the heavy atoms were all situated in one plane perpendicular to the c -axis (or nearly so). No systematic absences were observed. As the only element of symmetry which could be postulated would then be a mirror plane perpendicular to the c axis, the space group initially tried was $P6/m$. The location of the wolfram atoms could be treated as a two-dimensional problem. Approximate positions were obtained from a Patterson projection along $[001]$. The twelve wolfram atoms were found to be situated in two six-fold positions with the z parameter ≈ 0 . A least squares refinement of the heavy atom parameters alone resulted in a value of 0.243 of the discrepancy index:

$$R = \frac{\sum \left| |F_o(hkl)| - |F_c(hkl)| \right|}{\sum |F_o(hkl)|}$$

Although this was not quite as good an agreement as one might expect with heavy atoms, a difference Fourier synthesis was calculated on the basis of the structure factor signs thus obtained. The difference synthesis clearly showed that the two sets of wolfram atoms should be separated in the c direction. Accordingly, the non-centrosymmetric space group $P6$ was settled upon. A subsequent least squares refinement yielded an R -factor value of 0.146, a significantly lower value than gave the previous calculation.

Another three-dimensional difference Fourier synthesis was computed at points spaced 0.30 Å apart along the a axes and 0.38 Å apart along the c axis. This synthesis showed potassium to be located in a six-fold position at z approximately 0.50.

The positions of those oxygen atoms which were situated around wolfram in roughly the same plane ($z \sim 0$) were easily located. Three sixfold positions and one three-fold position were displayed on the Fourier maps. Mainly on spatial grounds the remaining oxygens were assumed to reside in three six-fold positions. The electron density in these regions was about half the value of the average height of the other oxygen peaks.

Table 2. Comparison between calculated and observed structure factors for $K_2W_4O_{13}$.

<u>h</u>	<u>k</u>	<u>l</u>	<u>F_{obs}</u>	<u>F_{calc}</u>	<u>h</u>	<u>k</u>	<u>l</u>	<u>F_{obs}</u>	<u>F_{calc}</u>
1	1	0	177	203	10	4	0	192	163
2	1	0	202	214	12	4	0	76	78
3	1	0	303	286	13	4	0	60	55
4	1	0	248	227	0	5	0	118	128
5	1	0	33	38	1	5	0	98	116
6	1	0	161	142	3	5	0	145	151
7	1	0	222	228	4	5	0	163	153
8	1	0	102	102	5	5	0	62	66
9	1	0	157	147	6	5	0	138	124
11	1	0	65	63	7	5	0	108	95
12	1	0	67	59	8	5	0	43	54
13	1	0	153	147	9	5	0	277	264
14	1	0	120	107	10	5	0	183	174
15	1	0	144	128	11	5	0	53	47
1	2	0	67	56	12	5	0	47	43
3	2	0	647	635	13	5	0	52	49
5	2	0	175	188	0	6	0	70	69
6	2	0	112	121	1	6	0	136	115
8	2	0	142	141	2	6	0	443	461
10	2	0	105	94	3	6	0	50	52
14	2	0	265	265	4	6	0	147	150
15	2	0	51	42	5	6	0	146	137
0	3	0	79	119	7	6	0	109	111
1	3	0	222	234	8	6	0	112	111
2	3	0	87	101	11	6	0	106	107
3	3	0	107	118	12	6	0	40	32
4	3	0	63	67	13	6	0	168	205
5	3	0	139	128	0	7	0	137	155
6	3	0	386	395	1	7	0	376	378
7	3	0	312	311	2	7	0	116	115
8	3	0	48	46	3	7	0	189	198
9	3	0	63	48	4	7	0	134	146
10	3	0	167	167	5	7	0	106	104
12	3	0	134	120	9	7	0	98	84
13	3	0	72	63	10	7	0	74	70
14	3	0	43	45	11	7	0	85	79
0	4	0	125	137	12	7	0	105	111
1	4	0	144	141	0	8	0	72	73
2	4	0	100	114	1	8	0	117	127
3	4	0	60	53	2	8	0	57	43
5	4	0	84	87	3	8	0	69	66
6	4	0	245	252	4	8	0	167	160
8	4	0	120	113	5	8	0	345	356

<u>h</u>	<u>k</u>	<u>l</u>	<u>F</u> _{obs}	<u>F</u> _{calc}	<u>h</u>	<u>k</u>	<u>l</u>	<u>F</u> _{obs}	<u>F</u> _{calc}
8	8	0	97	101	3	1	1	264	297
9	8	0	45	38	4	1	1	186	210
10	8	0	89	85	5	1	1	29	20
11	8	0	52	41	6	1	1	126	161
0	9	0	59	35	7	1	1	209	190
1	9	0	148	145	8	1	1	77	74
3	9	0	139	137	9	1	1	100	100
4	9	0	58	45	10	1	1	52	26
6	9	0	97	99	11	1	1	56	51
7	9	0	99	100	12	1	1	75	71
8	9	0	214	206	13	1	1	131	129
9	9	0	60	42	14	1	1	88	84
10	9	0	42	41	15	1	1	134	134
2	10	0	70	64	0	2	1	98	81
3	10	0	52	40	1	2	1	135	133
4	10	0	111	116	3	2	1	334	358
5	10	0	76	76	4	2	1	74	76
6	10	0	42	38	5	2	1	171	148
7	10	0	110	101	6	2	1	106	76
8	10	0	203	205	8	2	1	118	99
9	10	0	42	50	9	2	1	72	43
0	11	0	398	416	10	2	1	102	90
1	11	0	54	38	11	2	1	54	40
2	11	0	54	38	12	2	1	75	73
3	11	0	62	69	13	2	1	49	47
4	11	0	80	85	14	2	1	246	245
5	11	0	79	86	15	2	1	47	48
6	11	0	103	97	0	3	1	107	72
0	12	0	113	97	1	3	1	244	239
1	12	0	78	80	2	3	1	76	55
2	12	0	143	141	3	3	1	106	75
3	12	0	106	92	4	3	1	51	65
4	12	0	111	108	5	3	1	180	191
5	12	0	47	38	6	3	1	364	384
6	12	0	69	65	7	3	1	258	267
7	12	0	100	105	8	3	1	68	17
1	13	0	64	52	9	3	1	74	73
3	13	0	264	264	10	3	1	153	131
6	13	0	62	73	11	3	1	60	46
1	14	0	120	115	12	3	1	98	100
0	15	0	103	89	13	3	1	68	55
1	15	0	43	58	14	3	1	45	46
2	15	0	53	47	0	4	1	132	134
0	1	1	92	95	1	4	1	95	127
1	1	1	188	184	2	4	1	97	84
2	1	1	232	254	3	4	1	52	49

<u>h</u>	<u>k</u>	<u>l</u>	<u>F</u> _{obs}	<u>F</u> _{calc}	<u>h</u>	<u>k</u>	<u>l</u>	<u>F</u> _{obs}	<u>F</u> _{calc}
4	4	1	70	76	10	7	1	96	100
5	4	1	93	48	11	7	1	87	81
6	4	1	180	168	12	7	1	81	95
7	4	1	89	87	0	8	1	86	33
8	4	1	81	92	1	8	1	119	120
10	4	1	170	166	2	8	1	85	89
11	4	1	44	29	3	8	1	125	110
12	4	1	66	85	4	8	1	144	155
13	4	1	82	70	5	8	1	314	337
0	5	1	129	80	6	8	1	60	30
1	5	1	82	56	8	8	1	109	80
2	5	1	139	127	9	8	1	50	64
3	5	1	117	104	10	8	1	82	77
4	5	1	166	157	11	8	1	47	31
5	5	1	72	47	0	9	1	68	63
6	5	1	109	96	1	9	1	136	143
7	5	1	139	138	2	9	1	72	61
8	5	1	96	89	3	9	1	130	117
9	5	1	238	244	6	9	1	75	70
10	5	1	163	159	7	9	1	91	87
11	5	1	64	39	8	9	1	198	197
12	5	1	46	46	9	9	1	48	49
13	5	1	60	37	10	9	1	48	49
0	6	1	149	148	0	10	1	79	63
1	6	1	141	151	1	10	1	43	35
2	6	1	387	431	2	10	1	52	54
3	6	1	45	42	3	10	1	55	58
4	6	1	98	128	4	10	1	99	99
5	6	1	145	96	5	10	1	93	113
6	6	1	67	73	6	10	1	64	56
7	6	1	84	84	7	10	1	73	83
8	6	1	98	85	8	10	1	191	195
9	6	1	43	36	9	10	1	50	48
10	6	1	37	25	0	11	1	369	390
11	6	1	95	87	1	11	1	57	71
12	6	1	36	28	2	11	1	60	31
13	6	1	155	201	3	11	1	82	52
0	7	1	114	108	4	11	1	87	91
1	7	1	222	245	5	11	1	87	71
2	7	1	57	74	6	11	1	92	84
3	7	1	150	138	8	11	1	29	21
4	7	1	93	103	0	12	1	68	75
5	7	1	83	93	1	12	1	59	56
6	7	1	60	49	2	12	1	103	113
8	7	1	47	46	3	12	1	77	86
9	7	1	65	59	4	12	1	91	90

<u>h</u>	<u>k</u>	<u>l</u>	<u>F_{obs}</u>	<u>F_{calc}</u>	<u>h</u>	<u>k</u>	<u>l</u>	<u>F_{obs}</u>	<u>F_{calc}</u>
5	12	1	33	24	10	2	2	66	65
6	12	1	62	75	11	2	2	74	61
7	12	1	76	89	12	2	2	115	98
0	13	1	49	35	13	2	2	39	39
1	13	1	60	62	14	2	2	162	191
3	13	1	243	254	0	3	2	140	90
4	13	1	39	44	1	3	2	153	147
5	13	1	60	50	2	3	2	112	105
6	13	1	57	65	3	3	2	136	93
0	14	1	50	37	4	3	2	81	93
1	14	1	130	113	5	3	2	153	85
3	14	1	45	43	6	3	2	247	281
0	15	1	80	68	7	3	2	203	217
1	15	1	64	79	8	3	2	104	34
2	15	1	53	43	9	3	2	109	117
0	16	1	69	56	10	3	2	168	119
1	16	1	41	32	11	3	2	87	24
0	1	2	125	118	12	3	2	91	91
1	1	2	129	137	13	3	2	71	60
2	1	2	150	122	14	3	2	61	60
3	1	2	164	192	0	4	2	101	97
4	1	2	177	187	1	4	2	149	201
5	1	2	56	34	2	4	2	116	102
6	1	2	154	205	3	4	2	103	100
7	1	2	173	148	4	4	2	102	105
8	1	2	137	152	5	4	2	119	89
9	1	2	96	100	6	4	2	178	177
10	1	2	69	56	7	4	2	64	76
11	1	2	73	71	8	4	2	76	99
12	1	2	55	47	9	4	2	28	47
13	1	2	134	105	10	4	2	108	126
14	1	2	76	78	11	4	2	74	50
15	1	2	81	105	12	4	2	90	109
0	2	2	161	118	13	4	2	60	51
1	2	2	160	156	0	5	2	193	113
3	2	2	346	422	1	5	2	97	92
4	2	2	126	112	2	5	2	141	102
5	2	2	150	114	3	5	2	147	107
6	2	2	112	83	4	5	2	111	100
7	2	2	58	72	5	5	2	79	49
8	2	2	151	107	6	5	2	120	105
9	2	2	96	70	7	5	2	154	135

<u>h</u>	<u>k</u>	<u>l</u>	<u>F</u> _{obs}	<u>F</u> _{calc}	<u>h</u>	<u>k</u>	<u>l</u>	<u>F</u> _{obs}	<u>F</u> _{calc}
8	5	2	88	45	4	9	2	40	76
9	5	2	173	197	5	9	2	37	54
10	5	2	128	139	6	9	2	67	67
11	5	2	93	42	7	9	2	98	84
12	5	2	51	42	8	9	2	132	147
0	6	2	134	79	9	9	2	47	63
1	6	2	99	109	0	10	2	90	40
2	6	2	281	315	1	10	2	65	52
3	6	2	43	72	2	10	0	57	62
4	6	2	138	199	3	10	2	78	75
5	6	2	168	95	4	10	2	68	85
7	6	2	88	81	5	10	2	109	128
8	6	2	124	86	6	10	2	62	46
9	6	2	68	64	7	10	2	65	75
11	6	2	100	75	8	10	2	104	148
0	7	2	98	118	0	11	2	255	294
1	7	2	212	248	1	11	2	44	80
2	7	2	75	105	2	11	2	93	68
3	7	2	151	126	3	11	2	123	60
4	7	2	86	102	4	11	2	84	64
5	7	2	91	79	5	11	2	110	61
6	7	2	96	73	6	11	2	92	71
7	7	2	36	59	7	11	2	28	42
8	7	2	71	82	0	12	2	91	98
9	7	2	69	58	1	12	2	79	73
10	7	2	101	114	2	12	2	111	105
11	7	2	47	59	3	12	2	68	73
0	8	2	121	40	4	12	2	98	92
1	8	2	122	97	5	12	2	33	24
2	8	2	109	89	0	13	2	82	46
3	8	2	110	61	1	13	2	103	105
4	8	2	113	118	3	13	2	160	199
5	8	2	251	265	4	13	2	50	59
6	8	2	96	61	0	14	2	91	40
7	8	2	143	77	1	14	2	76	82
10	8	2	70	65	2	14	2	35	45
0	9	2	125	96	3	14	2	46	48
1	9	2	99	99	0	15	2	81	70
2	9	2	114	91	1	15	2	53	95
3	9	2	121	110					

The final least squares refinement with a full matrix program and individual isotropic temperature factors gave an R -factor of 0.134. Hughes' weighting function $w = 1/h^2 |F_o \text{ min}|^2$ for $|F_o| \leq h |F_o \text{ min}|$ and $w = 1/|F_o|^2$ for $|F_o| \geq |F_o \text{ min}|$ was used with the parameter h given the value 4. A comparison between calculated and observed F values is given in Table 2.

In addition to small spurious maxima in the electron density maps - easily dismissed as they lead to abnormal interatomic distances - there were two lower ones situated on the six-fold axis. The interpretation of either one of these as being a potassium site with the remaining five potassium atoms statistically distributed over the six-fold position could not be conclusively ruled out.

c. Description and discussion of the structure

A list of the structural parameters is given in Table 3. The temperature factors of the oxygens are somewhat anomalous which may be due to the difficulty in getting first class data from a crystal of unsuitable shape. No real physical significance can be attached to the temperature factors as the data have not been corrected for absorption.

Table 3. The crystal structure of $K_2W_4O_{13}$.

Space group $P6$ (No. 168 of the International Tables)

Cell content $3K_2W_4O_{13}$

12 W, 6 K and 36 O in 6(d): $\underline{x}, \underline{y}, \underline{z}; \bar{\underline{x}}, \underline{x}-\underline{y}, \underline{z}; \underline{y}-\underline{x}, \bar{\underline{x}}, \underline{z};$

$\bar{\underline{x}}, \bar{\underline{y}}, \underline{z}; \underline{y}, \underline{y}-\underline{x}, \underline{z}; \underline{x}-\underline{y}, \underline{x}, \underline{z}.$

3 O in 3(c): $\frac{1}{2}, 0, \underline{z}; 0, \frac{1}{2}, \underline{z}; \frac{1}{2}, \frac{1}{2}, \underline{z}$

Atom	$\underline{x} \pm \sigma(\underline{x})$	$\underline{y} \pm \sigma(\underline{y})$	$\underline{z} \pm \sigma(\underline{z})$	B
W(1)	.1780 \pm .0003	.2665 \pm .0003	.088 \pm .003	1.04 \pm .10
W(2)	.0899 \pm .0003	.4523 \pm .0003	0	.90 \pm .10
O(1)	.352 \pm .004	.036 \pm .004	.97 \pm .03	
O(2)	.029 \pm .006	.186 \pm .006	.19 \pm .03	
O(3)	.756 \pm .004	.378 \pm .004	.05 \pm .03	
O(4)	.636 \pm .008	.196 \pm .008	.18 \pm .04	Average value 3.0
O(5)	.066 \pm .010	.433 \pm .010	.56 \pm .07	
O(6)	0	1/2	.02 \pm .06	
O(7)	.161 \pm .013	.257 \pm .013	.57 \pm .099	
K	.497 \pm .002	.182 \pm .002	.51 \pm .02	3.4 \pm 0.6

The structure is built of WO_6 octahedra which are connected by shared corners to form six-membered rings in the xy plane. As a consequence of the short c axis, all octahedra also share corners in the z direction. A projection along 001 is given in Fig. 16 since the z parameter values of the top oxygens of the WO_6 octahedra obtained in different least squares refinements varied, the positions of these atoms were difficult to settle accurately. This effect may be the result if the wolfram atoms are in fact subject to "rattling" within the octahedra especially along the z direction.

Through the centres of the six-membered rings of octahedra are formed tunnels of infinite extension running in the direction of the short axis. This is a structural feature which several wolfram compounds have in common. The hexagonal wolfram bronzes (18) which are represented by a potassium bronze and also by rubidium and caesium bronzes have tunnel structures. In these compounds, the tunnels enclose the statistically distributed alkali ions. The pseudo-hexagonal wolfram trioxide (19), which has a superlattice due to the substitution of one molybdenum for every twelfth wolfram, contains six-edged empty channels running parallel to the c -axis which in this case has a length of 3.834 Å. Empty tunnels of infinite extension are also found in the wolfram oxide $W_{18}O_{49}$ (20).

In the tetrawolframate, the six potassium ions are probably located in a six-fold position, thus occupying interstices of a somewhat complicated shape. The one-fold position $00z$ would also be a plausible site in analogy with the conditions in wolfram bronzes. That this may in fact be the case is indicated by the difference Fourier syntheses and consequently by least-squares refinements based on that assumption. The potassium atoms may, thus, be distributed over a six-fold and one or two one-fold positions. That the two types of tunnel interstices arise in the tetrawolframate, only one of which is present in the structurally similar wolfram bronzes is due to the different manner of coupling of the WO_6 octahedra in the two structures. Whereas, in the latter structure the six-membered rings are

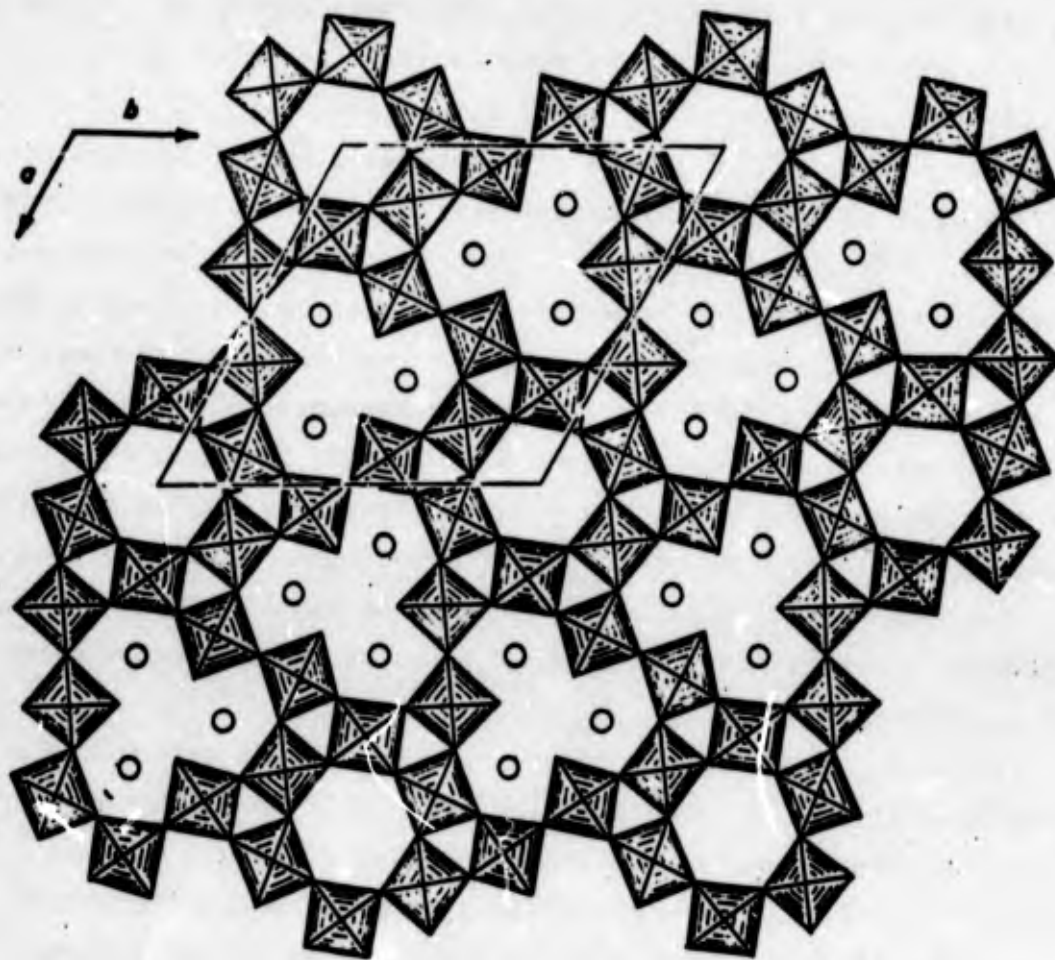


Figure 16. The structure of $K_2W_4O_{13}$ projected along the c -axis. The extent of one unit cell is indicated. The six-fold position of potassium is symbolized by circles.

sharing octahedra with adjacent rings, in the tetrawolframate the rings have no octahedra in common. They are more loosely connected sideways via a link of two corner-sharing octahedra. Additional tunnels of a more irregular shape are thus also formed in the structure (cf. Fig. 16).

4.3.3. Studies of the system $\text{Rb}_2\text{WO}_4\text{-WO}_3$

A thermal analysis of the system $\text{Rb}_2\text{WO}_4\text{-WO}_3$ has been made by Spitsyn and Kuleshov (21). The existence of di-, tri-, and hexawolframates was demonstrated. These phases melt incongruently at approximately 681° , 858° and 1045°C .

As the complexity of the isopolymolybdate and isopolywolframate anions studied so far seems to depend to a large extent on the nature of the alkali cation present, a comparison of the crystal structures of rubidium polywolframates to those of the potassium or sodium compounds may prove to be of interest. The presence of rubidium, which is one of the largest and least "polarizing" of the cations, would probably be conducive to the build-up of complex wolframate chains or a net-work with a high oxygen coordination number around wolfram. An analogous investigation of caesium polywolframates has not as yet been considered since one might anticipate that the presence of a heavy cation together with wolfram would tend to render the positions of the oxygen atoms as determined from X-ray investigations rather inaccurate.

Preparations have been made using Rb_2CO_3 and WO_3 as starting materials and heating appropriate mixtures of the components in platinum crucibles at temperatures slightly below the melting points of the desired products.

$\text{Rb}_2\text{W}_2\text{O}_7$ was prepared at 660°C . A lightly salmon-coloured crystalline product was obtained. The crystals are, however, poorly developed. The Guinier powder photograph does not indicate structural similarity with $\text{Na}_2\text{W}_2\text{O}_7$, the only diwolframate the structure of which has as yet been determined. Efforts are now being made to obtain larger crystals of $\text{Rb}_2\text{W}_2\text{O}_7$.

$\text{Rb}_2\text{W}_3\text{O}_{10}$ was prepared by heating of the reaction mixture to 840°C . A two phase system was obtained: a salmon-coloured phase identical with the one mentioned above which was interspersed with green prismatic crystals. The Guinier powder photograph of the latter was almost identical with a diffraction pattern of one of the preparations of $\text{K}_2\text{W}_3\text{O}_{10}$ (mentioned below) as well as with that of mixed compounds like e.g. $\text{K}_2\text{MoW}_2\text{O}_{10}$. This implies that the green crystals are in fact of the composition $\text{Rb}_2\text{W}_3\text{O}_{10}$. As the green prisms are easily separated from the mixture, attempts will be made to select a single crystal for data recording and subsequent structure determination.

Stoichiometric $\text{Rb}_2\text{W}_6\text{O}_{19}$ was heated to 1040°C and gave a dark green substance which under the microscope revealed the presence of prismatic crystals. The Guinier powder photograph consisted mainly of diffraction lines identical with those obtained from pure WO_3 previously heated to 800°C . A few extra lines appeared, however, and noticeable among these were two diffraction lines at low θ angles. Additional lines of similar character were also present on the powder photograph obtained from a $\text{Li}_2\text{O} + 4 \text{WO}_3$ mixture heated to 800°C . The product was suspected to contain what Hoermann (12) calls an octo-wolframate, a strongly acidic compound like $\text{Rb}_2\text{W}_6\text{O}_{19}$.

4.4. GLASSES AND CRYSTALLINE MATERIALS ON ARSENATE MOLYBDATE (WOLFRAMATE) BASIS

As described in previous reports (1,2) investigations have been performed within this research project on glasses prepared from the crystalline phases $\underline{\text{A}}\text{MoO}_2\text{PO}_4$ ($\underline{\text{A}} = \text{Na}, \text{Ag}$) (22,23) and NaWO_2PO_4 (22). The structural analogies often displayed by phosphorus(V) and arsenic(V) made it of interest to find out whether corresponding crystalline phases and a similar tendency to glass formation exist in the systems $\underline{\text{A}}_2\text{O}-\underline{\text{M}}\text{O}_3-\text{As}_2\text{O}_5$ ($\underline{\text{A}} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ or Ag ; $\underline{\text{M}} = \text{Mo}$ or W). The results so far obtained are somewhat preliminary in character.

4.4.1. Preparative work (Kaija Eistrat)

Preparations of the general composition $A_2O \cdot 2MO_3 \cdot As_2O_5$ were prepared by melting of alkali or silver carbonate (Baker Analyzed), arsenic pentoxide (Matheson, Coleman and Bell, Reagent) and molybdenum trioxide or wolfram trioxide (Mallinckrodt, analytical reagent) in a platinum crucible for two or three minutes at a temperature of about $1050^\circ C$. After rapid quenching, the character of the products was tested by visual inspection and microscopically, and also by means of X-ray powder techniques. The compositions were checked by weighing of the samples before and after the heat-treatment. Vitreous products were thus obtained for all the samples except $Li_2O \cdot 2WO_3 \cdot As_2O_5$. Additional heat-treatment of the vitreous materials at $500^\circ C$ for periods up to 7 days resulted in devitrification of all the samples containing molybdenum and also of the preparations $A_2O \cdot 2WO_3 \cdot As_2O_5$ ($A = Na, K$ and Ag). Further data concerning the results of the preparative studies are summarized in Table 4.

Table 4. Data for preparations of general composition $A_2O \cdot 2MO_3 \cdot As_2O_5$ ($A = Li, Na, K, Rb, Cs$ or Ag ; $M = Mo$ or W).

Atom <u>A</u>	Character * and colour ** of the product after:			
	quenching a melt from $1050^\circ C$ <u>M</u> = Mo	quenching a melt from $1050^\circ C$ <u>M</u> = W	heat-treatm. $500^\circ C$ 7 days <u>M</u> = Mo	heat-treatm. $500^\circ C$ 7 days <u>M</u> = W
Li	G, green	C, white	C, white	C, white
Na	G, green	G, yellow	C, white	C, white
K	G, brown	G, yellow	C, white	C, white
Rb	G, brown	G, yellow	C, white	C, white
Cs	G, brown	G, light yellow	C, white	C, white
Ag	G, dark brown	G, green-yellow	C, light yellow	C, white

* G = glasses or C = crystalline material.

** Given for the materials as powders.

The structural study undertaken for the phase $\text{Li}_2\text{O} \cdot 2\text{MoO}_3 \cdot \text{As}_2\text{O}_5$ (cf. below) made it of interest to investigate the range of glass formation and also the phase conditions of the lithium molybdate arsenate system in some more detail. By varying of the proportions of the constituents and treating of the mixtures in the way described above it was found that glasses of rather different compositions could be easily obtained in this system. The colour of these materials, the vitreous character of which was verified by X-ray techniques, varied from brownish to greenish. Upon further heat-treatment at 500°C for a week, crystallisation was found to have taken place in all the samples investigated with the exception of a green preparation of the approximate composition $\text{Li}_2\text{O} \cdot 2\text{MoO}_3 \cdot 2\text{As}_2\text{O}_5$ which still retained its vitreous character. The powder patterns of the devitrified samples, which represented $\text{MoO}_3:\text{As}_2\text{O}_5$ ratios ranging from 1:4 to 2:1 and also different contents of Li_2O , showed the presence of a considerable number of ternary phases. Further studies on this matter are in progress.

A structural study is now being performed on the crystalline phase obtained by devitrification of the glass of composition $\text{Li}_2\text{O} \cdot 2\text{MoO}_3 \cdot \text{As}_2\text{O}_5$. The composition of the colourless crystals is likely to be the same as that of the glass, i.e. $\text{LiMoO}_2\text{AsO}_4$. The symmetry is orthorhombic or pseudorhombic. Further work is in progress.

4.5. STUDIES ON PHOSPHATES OF ZIRCONIUM AND URANIUM

One of the aims of the present research has been to study the linking of $\underline{\text{M}}\text{O}_6$ octahedra and $\underline{\text{M}}'\text{O}_4$ tetrahedra and their role as structural units in glasses and crystals. Most of this work has, as far as the $\underline{\text{M}}$ atoms are concerned, dealt with Mo and W compounds while in addition to P and As, as $\underline{\text{M}}'$ atoms have also been included, transition elements such as Mo, W and V. A group of substances of interest from the point of view of further varying the character of the $\underline{\text{M}}$ atom includes the so-called Peyronel phases, i.e. $\underline{\text{M}}\text{P}_2\text{O}_7$ ($\underline{\text{M}}$ = tetravalent atoms ranging from Si to U and Th). Recent studies

on this interesting family of compounds have shown that the structure originally reported by Peyronel and coworkers (24,25) does not cover all the details of the atomic arrangement but represents a substructure. The ZrP_2O_7 phase, which is now being investigated at this Institute, actually has a unit cell 27 times larger than the one previously reported. The symmetry is lower than cubic. It is probably orthorhombic.

The very complicated superstructures thus found for the Peyronel phases has made it seem desirable to undertake studies on some related phases with less complex structures. The work in this area has so far comprised $NaZr_2(PO_4)_3$ and $U(PO_3)_4$.

4.5.1. The structure of $NaZr_2(PO_4)_3$ (Lars-Ove Hagman)

Within the present study the compounds $NaZr_2(PO_4)_3$, $NaTi_2(PO_4)_3$ and $NaGe_2(PO_4)_3$ have been synthesized and found to be isomorphous. According to data reported by Sljukić et al. (26) further compounds of this stoichiometry, viz. zirconium and hafnium phosphates of all the alkali metals, should also belong in this structural family. The sodium zirconium phosphate was chosen for a single-crystal X-ray study of this extensive isomorphous series. MO_6 octahedra and PO_4 tetrahedra, linked by corners to form a threedimensional network were thus found to represent the structural principle of these compounds. A detailed account of the investigation have been submitted as a Special Technical and Scientific Report, which is also enclosed as Appendix IV of this report.

4.5.2. The structure of $U(PO_3)_4$ (Ann Kopwillem)

a. Experimental

$U(PO_3)_4$ was prepared by heating U_3O_8 with excess $(NH_4)_2HPO_4$ to $1000^\circ C$. The crystalline powder thus obtained which was somewhat heterogeneous was further heated with conc. orthophosphoric acid at $600^\circ C$. In this way green single crystals of $U(PO_3)_4$ were obtained which could be easily separated from the residue. Analyses, density measurements and other methods of preparation are described by Colani (27), Burdese and Borlera (28), Douglas (29) and Baskin (30).

The powder pattern was easily interpreted assuming an orthorhombic unit cell. Values for the cell dimensions were calculated from a photograph taken with strictly monochromatized CuK_α radiation in a Guinier-Hägg type focusing camera. Potassium chloride was used as an internal standard (see Table 5). The unit cell dimensions are (25°C):

$$\underline{a} = 6.9106 \pm 0.0009 \text{ (\AA)}$$

$$\underline{b} = 14.9399 \pm 0.0003 \text{ (\AA)}$$

$$\underline{c} = 8.9868 \pm 0.0007 \text{ (\AA)}$$

$$\underline{V} = 927.8 \text{ (\AA}^3\text{)}$$

From rotation and Weissenberg photographs ($\underline{hk0-hk5}$, $\underline{0kl-4kl}$) of a single crystal with the dimensions 0.032 mm (in the direction of the \underline{a} axis) x 0.018 mm (\underline{b}) x 0.021 mm (\underline{c}) - taken with CuK radiation, it was concluded that the crystals have the Laue symmetry \underline{mmm} . The reflections systematically absent are $\underline{0kl}$ with $\underline{k} = \text{odd}$, $\underline{h0l}$ with $\underline{l} = \text{odd}$ and $\underline{hk0}$ with $\underline{h+k} = \text{odd}$, which is characteristic of the space group \underline{Pbcn} .

The reflections were recorded photographically with multiple film technique. The relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times. A total of 321 independent reflections were assigned an intensity.

Practically all the computational work involved in this study, including refinement of the lattice constants (Program No. 6018), absorption correction (No. 6019), Lorentz polarization correction (No. 6024), Fourier summations (No. 6015), least-squares refinement (No. 6023) and calculation of interstomic distances (No. 6016) were performed on the electronic computers FACIT EDB and TRASK. The numbers refer to the list of crystallographic computer programs (3).

When determining the \underline{F}^2 values, the linear absorption coefficient, $\mu = 670.8 \text{ cm}^{-1}$, was derived from atomic absorption coefficients given by Victoreen (31).

Table 5. X-ray powder data observed for $U(PO_3)_4$.
 $CuK\alpha_1$ radiation. $\lambda_{CuK\alpha_1} = 1.54050 \text{ \AA}$.

<u>h</u> <u>k</u> <u>l</u>	$10^5 \sin^2 \theta$ obs	$10^5 \sin^2 \theta$ calc	<u>I</u>
1 1 0	1511	1511	S
1 2 1	1799	1801	S
1 1 1	2247	2247	S
0 0 2	2949	2943	VW
1 2 1	3047	3045	VW
1 3 0	3640	3641	VS
0 2 2	4005	4009	M
1 0 2	4189	4188	M
1 3 1	4374	4377	M
1 1 2	4453	4454	VS
1 3 2	6585	6584	M
2 2 1	6772	6779	S
0 4 2	7197	7204	VS
0 2 3	7690	7688	S
2 0 2	7921	7921	M
1 1 3	8129	8133	M
1 5 1	8628	8637	M
2 4 0	9239	9238	M
2 3 2		10317	
0 6 1	10298	10321	VW
1 5 2		10844	
0 4 2	10867	10883	VW
2 4 2		12181	
3 1 1	12186	12202	M
2 2 3	12661	12665	W
1 1 4	13288	13284	W
1 5 3	14531	14523	S
2 6 1	15289	15299	W
1 3 4	15411	15414	S
3 4 1		16196	
0 6 3	16201	16208	W
3 3 2	16534	16540	W
2 0 4	16739	16751	W
1 7 2	17233	17234	S
2 6 2	17503	17506	VW
3 5 1	18591	18592	W
0 2 5	19451	19461	W
1 1 5		19907	
4 0 0	19919	19911	M
4 2 0		20976	
2 4 4	21004	21011	W
1 9 1	23546	23547	W
2 2 5	24449	24439	VW
2 8 2	24940	24962	VW
3 3 4	25353	25370	VW
1 7 4	26075	26064	VW
1 5 5	26306	26097	VW
4 4 2	27132	27114	VW
0 6 5		27981	
1 1 6	27999	28001	VW

b. Investigation of the structure

The structural analysis performed on the basis of the data mentioned above included investigations of the Patterson and electron density functions and least-squares refinement of the atomic arrangement thus obtained. In this way result given in Table 6 was arrived at, corresponding to an R-value of 13 %.

Table 6. The substructure of $U(PO_3)_4$.

Space group: No. 60 Pbcn.

Unit cell dimensions: a = $6.9106 \pm 0.0009 \text{ \AA}$

b = $14.9399 \pm 0.0003 \text{ \AA}$

c = $8.9868 \pm 0.0007 \text{ \AA}$

Cell content: 4 $U(PO_3)_4$

4 U and 4 O_6 in 4(c): $\pm(0, y, \frac{1}{4}); (\frac{1}{2}, \frac{1}{2}+y, \frac{1}{4})$

8 P_1 , 8 P_2 , 8 O_1 , 8 O_2 , 8 O_3 , 8 O_4 , 8 O_5 and 4 O_7 in 8(d):

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

Atom	<u>x</u> ± σ(<u>x</u>)	<u>y</u> ± σ(<u>y</u>)	<u>z</u> ± σ(<u>z</u>)	<u>B</u> ± σ(<u>B</u>) Å ²
U	0	0.1379 ± 0.0002	1/4	1.17 ± 0.05
P_1	0.346 ± 0.003	0.314 ± 0.001	0.139 ± 0.005	1.53 ± 0.38
P_2	0.287 ± 0.003	0.017 ± 0.001	0.520 ± 0.004	1.54 ± 0.46
O_1	0.231 ± 0.008	0.246 ± 0.003	0.195 ± 0.007	
O_2	0.915 ± 0.009	0.264 ± 0.004	0.998 ± 0.009	
O_3	0.211 ± 0.011	0.399 ± 0.005	0.157 ± 0.014	
O_4	0.737 ± 0.011	0.056 ± 0.004	0.139 ± 0.013	Average 2.19
O_5	0.338 ± 0.014	0.549 ± 0.005	0.071 ± 0.015	
O_6	0	0.855 ± 0.004	1/4	
O_7	0.014 ± 0.022	0.519 ± 0.005	0.027 ± 0.017	

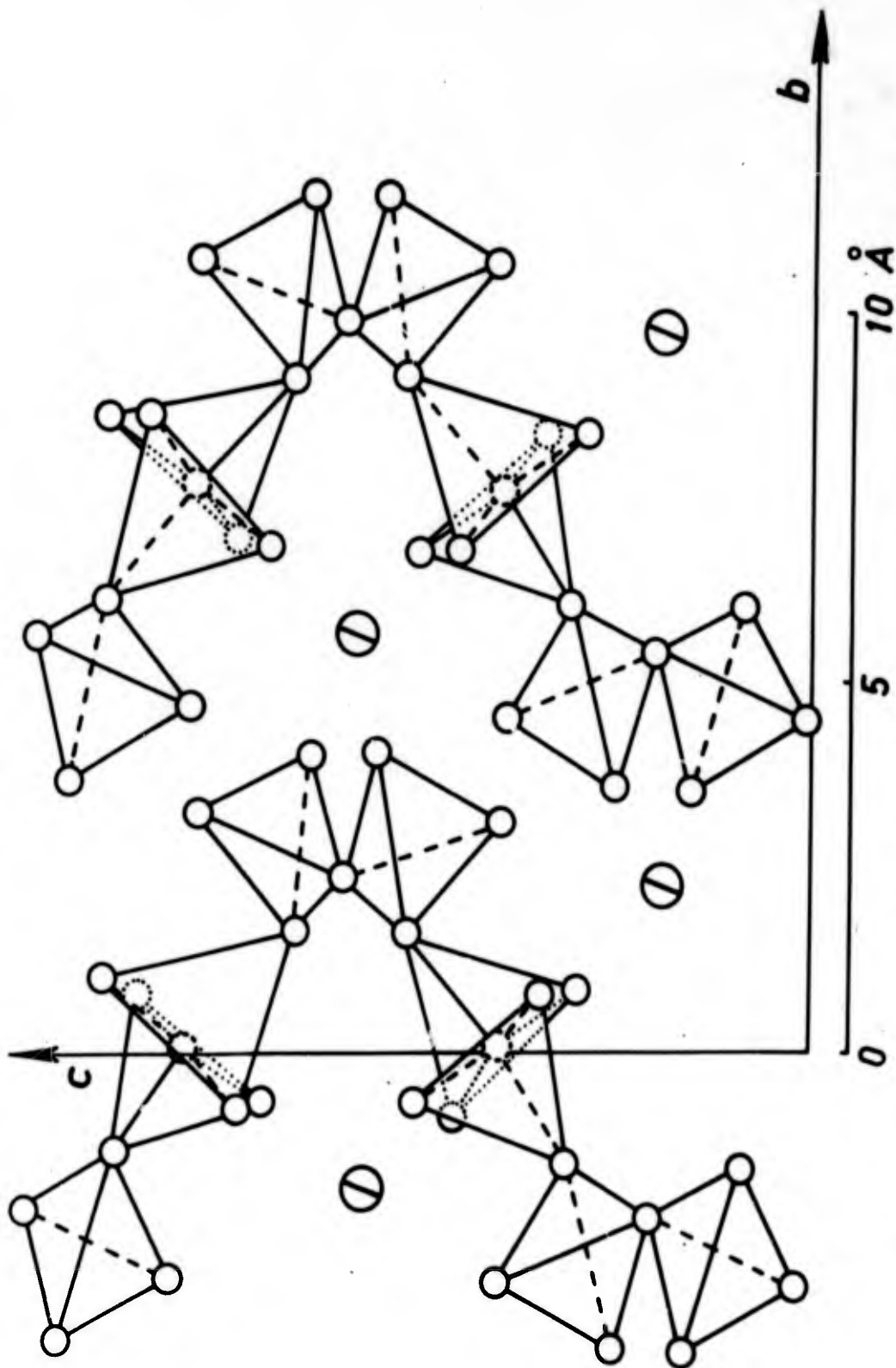


Figure 17. Schematic drawing of the crystal structure of $U(PO_3)_4$. Small circles denote oxygen atoms and big, lined circles uranium atoms. The phosphorus atoms in the PO_3^- -chains have not been indicated.

An inspection of the positional and "thermal" parameters as obtained in the course of the refinement suggests that the structure is essentially correct but casts some doubt on the arrangement of the O_7 atoms. The high "thermal" parameter value of this atom indicated the presence of either a disorder or a superstructure. The former alternative was considered less probable as it was likely to effect some disorder in the arrangement of neighbouring O atoms. The possibility of a superstructure was thus carefully tested by close inspection of single-crystal photographs registered with very ample exposure, viz. for periods ten times the normal ones. In this way very faint reflections were disclosed which required a doubling of the a axis. This observation actually confirms the unit cell size reported by Baskin (30).

So far a refinement of the structural details of the superstructure cannot be undertaken due to the unfavourable proportion between the number of observed independent reflections and the number of atomic parameters.

However, the picture given by the analysis of the substructure provides some essentials about the structure principles of $U(PO_3)_4$ (cf. Fig. 17). Thus the oxygen arrangement around uranium is eight-fold in a somewhat distorted square antiprism. Metaphosphate chains form spirals with a repeat unit of 8 PO_4 -tetrahedra.

4.6. STUDIES ON TERNARY OXIDE SYSTEMS CONTAINING VANADIUM AND MOLYBDENUM OR WOLFRAM

Recent studies conducted at this Institute and elsewhere have given ample evidence that the coordination numbers in oxide compounds of vanadium, molybdenum, wolfram and also some other transition elements may differ quite a lot dependent on the structural character of the particular oxide. All of these metals may occur in \underline{MO}_4 tetrahedra or \underline{MO}_6 octahedra but such polyhedra often deviate considerably from regularity. Arrangements of atoms better described as intermediates between tetrahedra and octahedra are frequently met with. In the phosphates of transition elements investigated within this program the P

atoms invariably occur in a tetrahedral environment. The present investigations of the ternary oxide systems with vanadium and molybdenum or wolfram have been undertaken in order to find out how variations in composition and oxidation number affect the coordination conditions of these transition elements. It is thus to be looked upon as an extension of the research described above on alkali polymolybdates and polywolframates.

4.6.1. The molybdenum vanadium oxide system (Lars Kihlberg)

The results of an extensive phase analysis investigation of the Mo-V-O system at 600°C are summarized in Fig. 18. Starting from reagent grade MoO₃ and V₂O₅, batches of MoO₂ and V₂O₃ respectively were prepared by reduction with hydrogen. Appropriate mixtures of the various oxides were heated for periods of several days in sealed evacuated silica or platinum capsules at 600°C.

Upon quenching, the ternary oxide products were investigated by X-ray powder techniques. The ternary phases thus found to exist are listed in Table 7 which also presents some crystallographic characteristics.

The binary border-line systems Mo-O and V-O have been studied in considerable detail by members of this and associated groups and were consequently not included in the present investigation.

The crystal structures of the phases VOMoO₄ and V₂Mo₃ were determined some time ago by Eick and the present author (32, 33). The structure of (Mo_{0.3}V_{0.7})₂O₅ which may be considered as the end member of a structurally related series of compounds, extending from the binary composition V₂O₅ has also been solved. The results of this study are described in Appendix III of this report and in a recent article (34). A discussion of the structural relations existing between V₂O₅, (Mo_{0.3}V_{0.7})₂O₅ and V₂MoO₈ is also given in this article.

The phase (Mo_{0.93}V_{0.07})₅O₁₄ has been found to be isostructural with Mo₅O₁₄ (35) but with somewhat different unit cell parameters. The binary Mo₅O₁₄ phase has never been obtained at temperatures ex-

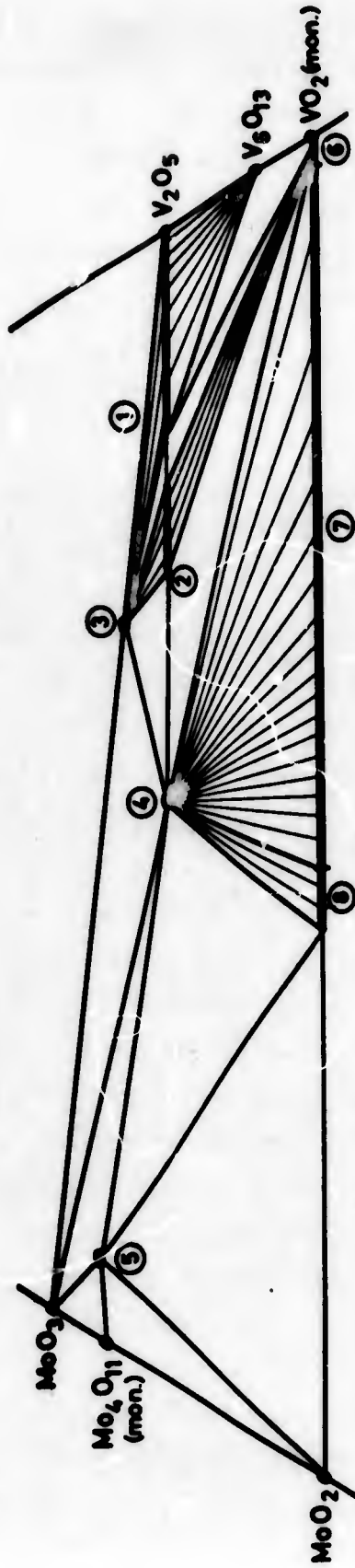


Figure 18. Part of the Mo-V-O phase diagram as obtained from X-ray powder diffraction photographs taken at room temperature after heat treatment of the samples at 600°C. The intermediate phases are designated by numbers which are explained in table

Table 7. Intermediate phases in the Mo-V-O system forming at about 600°C.

Designation in Fig.	Composition	Symmetry	Unit cell dimensions	Remarks
1	$(\text{Mo}_x\text{V}_{1-x})_2\text{O}_5$ $0 \leq x < \sim 0.17$	Orthorhombic	See Fig. 19	V_2O_5 structure. The upper limit of x is approximate. The powder patterns of samples around x=20 are complex and may possibly indicate the presence of a phase with a more complicated struct.
2	$(\text{Mo}_x\text{V}_{1-x})_2\text{O}_5$ $\sim 0.23 < x < 0.30$	Monoclinic	See Fig. 19	Structure related to that of V_2O_5 (34). Lower limit of x is approximate, see above.
3	MoV_2O_8	Monoclinic	a = 19.40 Å b = 7.258 Å c = 4.117 Å β = 90.34°	Structure related to those of V_2O_5 and $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ (33). May have a narrow homogeneity range.
4	VOMoO_4	Tetragonal	a = 6.6078 Å c = 4.2646 Å	Structure see (32). May have a narrow homogeneity range.
5	$(\text{V}_{0.07}\text{Mo}_{0.93})_5\text{O}_{14}$	Tetragonal	a = 22.85 Å c = 3.990 Å	Mo_5O_{14} structure (35).
6	$(\text{Mo}_x\text{V}_{1-x})\text{O}_2$	Monoclinic	a = 7.751 Å b = 4.526 Å c = 5.383 Å β = 122.6°	Low- VO_2 structure (distorted rutile). The upper limit of x is uncertain but not greater than 0.02
7	$(\text{Mo}_x\text{V}_{1-x})\text{O}_2$ $\sim 0.03 < x < 0.55$	Tetragonal	See Fig. 20	Rutile-type struct.
8	$(\text{Mo}_x\text{V}_{1-x})\text{O}_2$ $0.55 < x < 0.60$	Orthorhombic	a = 6.69 Å b = 6.62 Å c = 2.84 Å	Slightly distorted rutile structure.

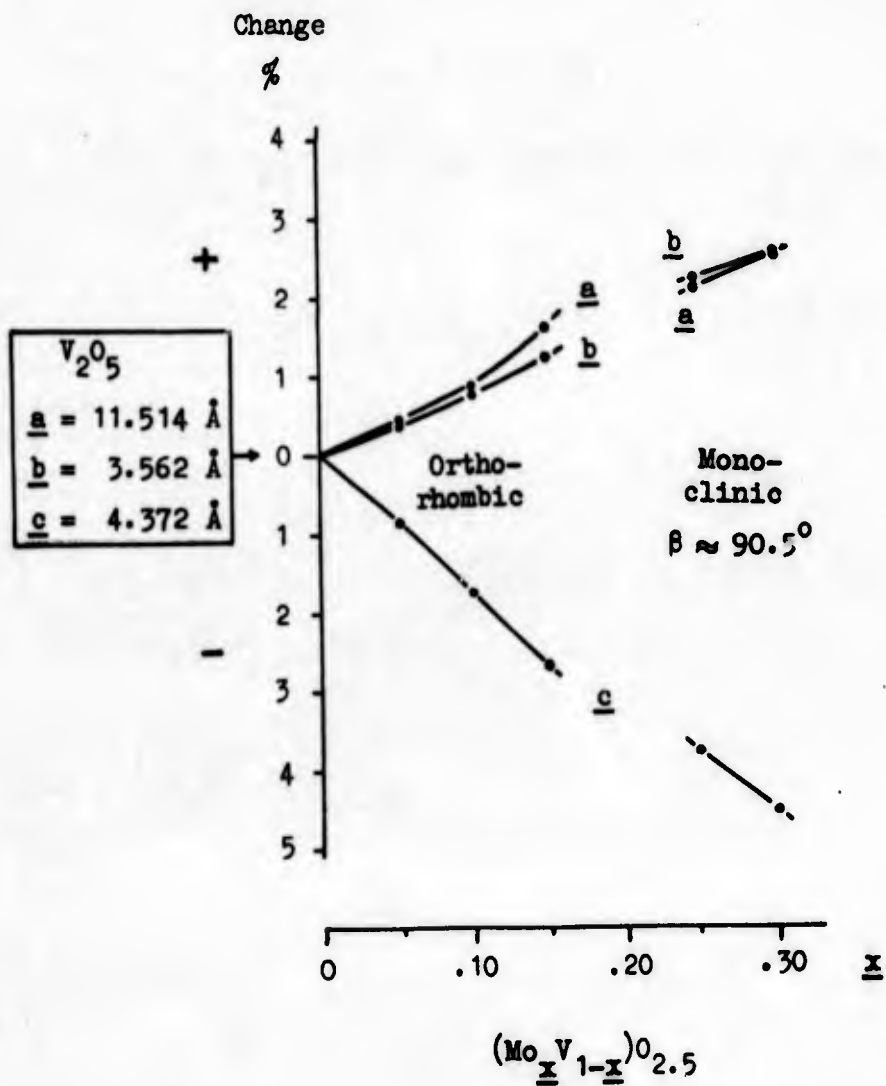


Figure 19. The change of the unit cell parameters compared to those of V_2O_5 plotted versus composition for phases $(Mo_x V_{1-x})_{0.25}$.

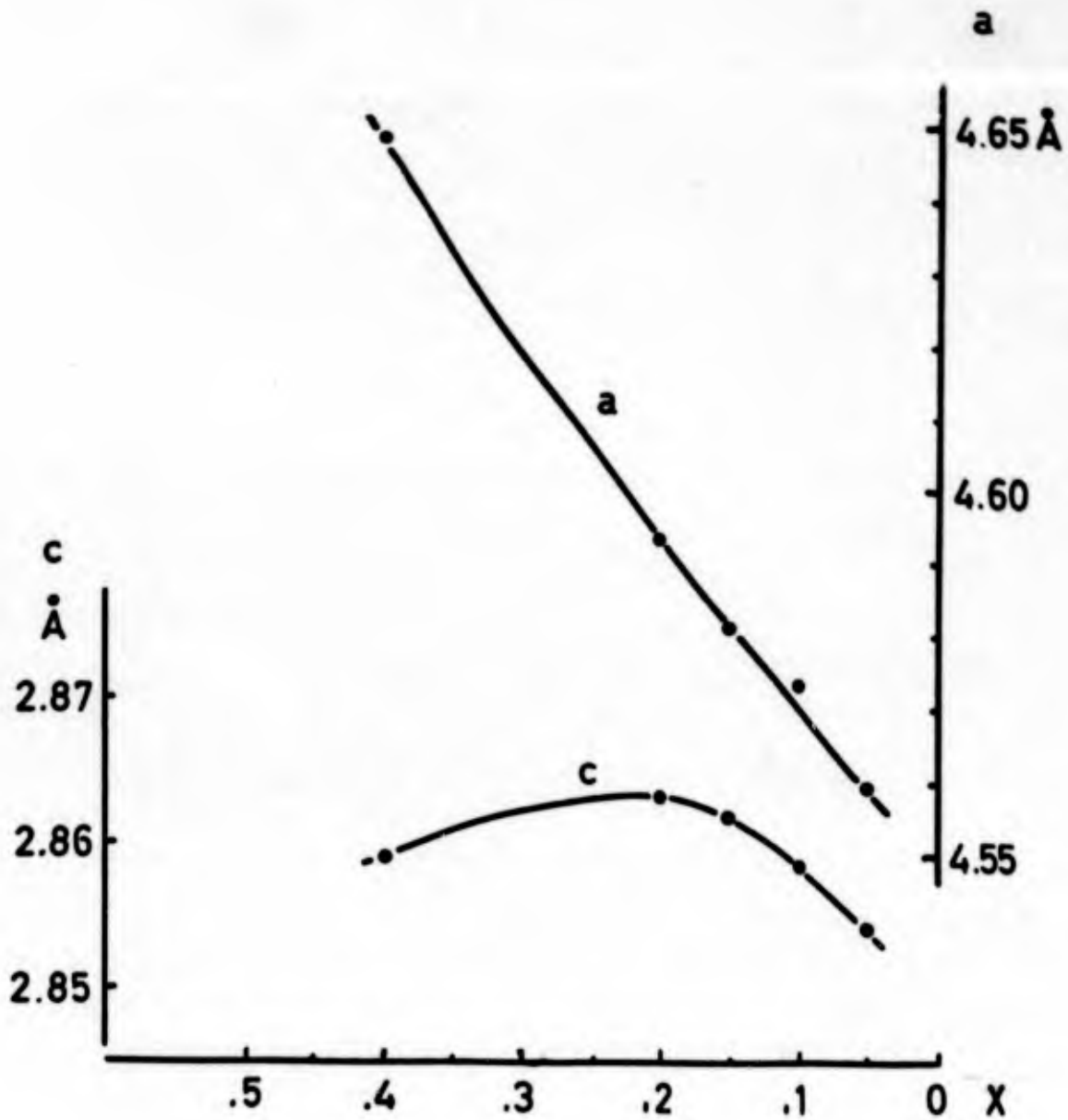


Figure 20. The variation of the unit cell parameters with composition for rutile-type phases $(\text{Nb}_x\text{V}_{1-x})\text{O}_2$.

ceeding 520°C. The ternary compound prepared at 600°C seems to have a very narrow compositional range of stability.

The present studies on the Mo-V-O system have given further evidence of the variability of the coordination numbers of vanadium and molybdenum. The structural elements present in the family comprising V_2O_5 , $(Mo_{0.3}V_{0.7})_2O_5$ and V_2MoO_8 and which also includes $R-Nb_2O_5$ (36) and Nb_3O_7F (37), may be described as \underline{MO}_6 octahedra showing a more or less marked distortion. The ternary oxide of Mo_5O_{14} type likewise contains distorted \underline{MO}_6 octahedra and also \underline{MO}_7 pentagonal bipyramids. The structure of $VOMo_4$ is of a particular interest, being isomorphous with the molybdenum oxide phosphate $MoOPO_4$. Thus, the former contains distorted VO_6 octahedra and fairly regular MoO_4 tetrahedra.

4.6.2. The wolfram vanadium oxide system (Mats Israelsson and Lars Kihlberg)

The present study of the phase relations in the W-V-O system have essentially been restricted to the regions which according to studies by Freundlich et al. (38) contain ternary phases. The preparative work was made in a way analogous to the one described above for the Mo-V-O system. Temperatures within the range 700-1100°C were used when preparing the samples.

The existence of two ternary phases has been demonstrated within the present work. The compositions found are fairly close to $W_{0.375}V_{0.625}O_{2.5}$ (temperature of formation 800-1000°C) and $V_{0.35}W_{0.65}O_{2.5}$ (800°C). These compositions deviate only slightly from those reported by Freundlich et al. (38). The crystal structures of the two phases have been determined from three-dimensional X-ray data.

The structure of $W_{0.375}V_{0.625}O_{2.5}$, which has so far been refined to an R -value of 0.07, may be described as belonging in the V_2O_5 -type family (cf. Fig. 21). Thus, the structural elements are distorted

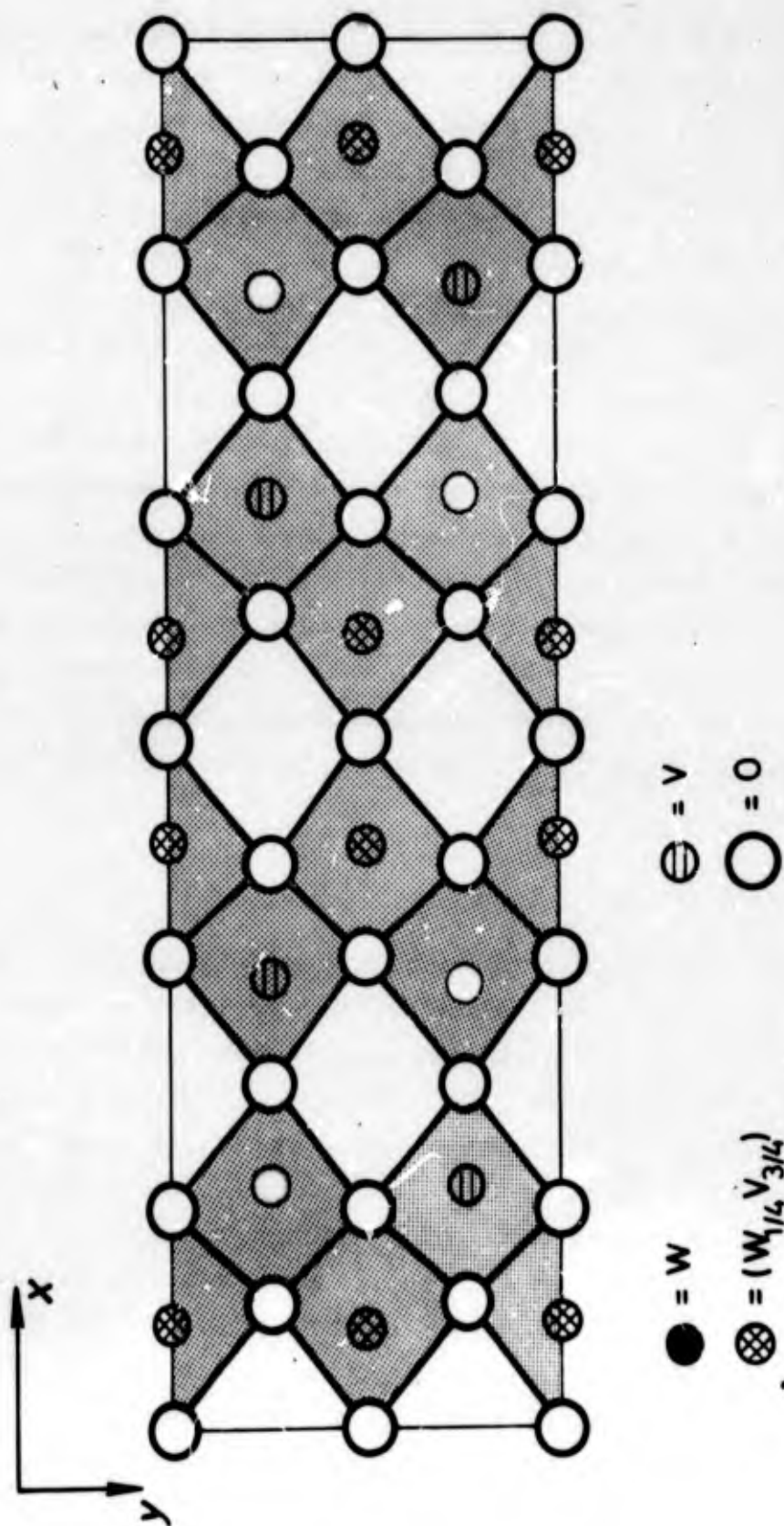


Figure 21. The crystal structure of the monoclinic wolfram vanadium oxide, $W_{0.375}V_{0.625}O_2$, viewed along the short c -axis. The oxygen atoms approximately above and below each metal atom along the line of sight have been omitted.

\underline{MO}_6 octahedra joined by edges and corners to form layers, the latter being linked together by additional sharing of corners. The atomic positional parameters are fairly close to those found in $(\underline{Mo}_{0.3}\underline{V}_{0.7})_2O_5$ (cf. Appendix III) but a partially ordered distribution of the W and V atoms gives rise to a superstructure which manifests itself in a doubling of both the \underline{a} and \underline{b} axes.

The tetragonal structure of $\underline{W}_{0.35}\underline{V}_{0.65}O_{2.5}$ is illustrated in Fig. 22. The structure contains \underline{MO}_6 octahedra, some of which, however, are considerably distorted in such a way that the shape approaches that of a \underline{MO}_4 tetrahedral polyhedron. The \underline{MO}_6 octahedra are joined by corners to form blocks of infinite extension along the tetragonal axis and having a cross section of 4x4 polyhedra. The blocks are mutually linked by octahedra sharing edges. The structure has been refined to an \underline{R} -value of 0.062. This has been achieved under the assumption of different W/V ratios on the three crystallographically different metal atom positions. The atomic distribution thus arrived at corresponds to the least divergence of the \underline{B} values ("thermal parameters") of the various metal atom positions.

4.7. STUDIES ON COPPER WOLFRAM OXIDES (Lars Kihlberg)

The studies on copper wolfram oxides described below have been conducted in parallel with the present research project but essentially as part of other research, performed by the present author in cooperation with E. Gebert. As the results obtained, however, have been found to be of considerable interest and to give further illustrations of the structural behaviour of wolfram in oxide compounds it has been thought worth-while to report briefly on this work here.

Considerable effort has been devoted to phase analysis studies on the Cu-W-O system. Experimental difficulties, however, not yet overcome have so far prevented the attaining of a complete picture of the phase conditions of this system. The work has instead been concentrated on structural studies on the two ternary phases observed, viz. \underline{CuWO}_{4-x}

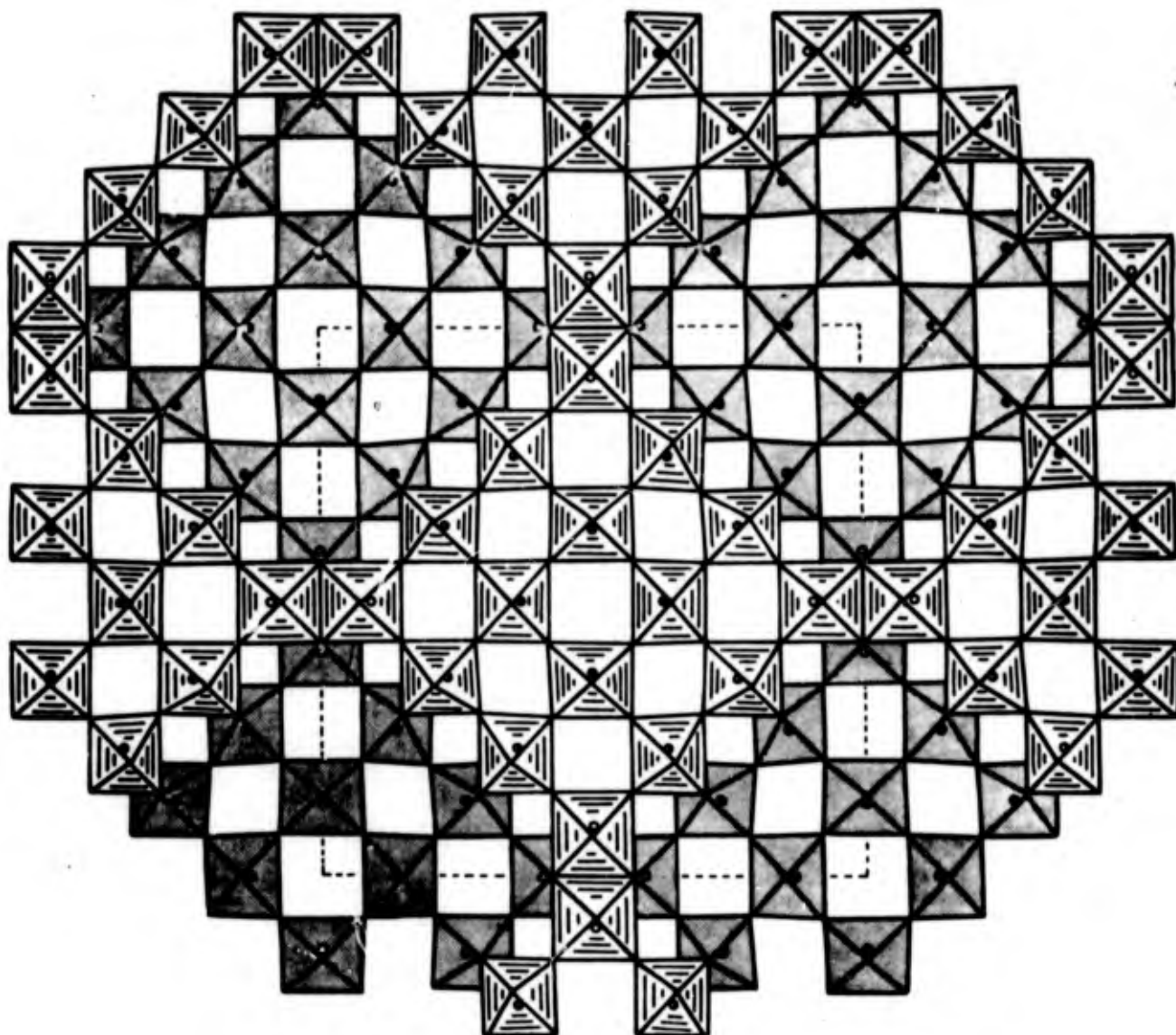


Figure 22. The crystal structure of the tetragonal wolfram vanadium oxide, $W_{0.35}V_{0.65}O_{2.5}$, viewed along the tetragonal axis. The structure is regarded as built up of MO_6 octahedra as two levels (light and dark, respectively), joined by corners to identical octahedra above and below. The extension of the unit cell is indicated by broken lines.

and Cu_3WO_6 . The structures have been solved and refined on the basis of accurate three-dimensional single-crystal data registered by means of a diffractometer. The final R -values are 0.038 for CuWO_{4-x} and 0.065 for CuWO_6 .

CuWO_{4-x} has been found to be of a distorted wolframite type of structure. The triclinic unit cell dimensions are

$$\begin{aligned} \underline{a} &= 4.703 \text{ \AA}, & \underline{b} &= 5.839 \text{ \AA}, & \underline{c} &= 4.878 \text{ \AA} \\ \alpha &= 91.68^\circ, & \beta &= 92.47^\circ, & \gamma &= 82.81^\circ \end{aligned}$$

The divergence from the normal monoclinic wolframite-type of structure lies mainly in the deviation of the angle γ from 90° . The WO_6 octahedra are distorted in an irregular way, which is reflected in the W-O distance of 1.76, 1.81, 1.84, 1.98, 2.03 and 2.20 \AA . The environment of copper is also an octahedral one but of a marked 4+2 character, the former distances ranging from 1.96 to 2.00 \AA and the two latter being about 2.4 \AA . The B -values of the oxygens all have similar but rather high values ($2.5 \pm 0.1 \text{ \AA}^2$) which may indicate some connection with the deficiency in oxygen of this compound as compared with the stoichiometry required by an ideal structure of this type.

The structure of Cu_3WO_6 is of a new type. The cubic unit cell ($\underline{a} = 9.799 \text{ \AA}$) contains eight formula units. The arrangement of oxygens around wolfram represents a 3+3 type distortion of an octahedron. There is no mutual linking between the WO_6 groups. The coordination around copper is of a rather rare type, viz. a triangular bipyramid. Further details on this structure are given in Appendix V of this report.

4.8. MAGNETIC PROPERTIES OF MOLYBDENUM AND WOLFRAM OXIDE PHOSPHATES
(Gunilla Barvling and Lars Kihlberg)

The apparatus for magnetic measurements described above (sect. 2.3) has recently been taken into use for investigations of the magnetic properties of various substances studied within this program. So far this work has been mainly concerned with vitreous and crystalline oxide phosphates of molybdenum and wolfram. Measurements have, however, also been performed on samples of disodium diwolframate. The very plausible diamagnetic character of this compound has been confirmed for the crystalline material as well as for glasses of different thermal treatment. The χ_g values obtained are in the region $-0.8 \cdot 10^{-6}$ to $-1.2 \cdot 10^{-6}$ cgs units.

The data obtained for some molybdenum and wolfram oxide phosphates are summarized in Table 8.

Table 8. Magnetic data for molybdenum and wolfram oxide phosphates $\underline{M}O_{3-x} \cdot yP_2O_5$ (\underline{M} = Mo or W)

Compound	Composition		Magnetic character	χ_g cgs units
	\underline{x}	\underline{y}		
MoOPO ₄ , cryst.	1/2	1/2	Paramagnetic	$\begin{cases} 2 \cdot 10^{-6} & (298^\circ K) \\ 8 \cdot 10^{-6} & (100^\circ K) \end{cases}$
- " - , glass	0.23	0.44	Diamagnetic	
W ₂ O ₃ (PO ₄) ₂ , cryst.	0	1/2	- " -	$-0.8 \cdot 10^{-6}$
- " - , glass	0.01	0.49	- " -	$-1.2 \cdot 10^{-6}$

The diamagnetic character of the crystalline and vitreous wolfram oxide phosphates is in concordance with the fully or very nearly fully oxidized state of wolfram in these substances.

The values given above for crystalline MoOPO₄ are not very accurate as the amount of substance available was an extremely small one.

The paramagnetic character of this material is, however, secured by the measurements. This is in full accordance with the evidence given by the structural investigation previously reported (39). The arrangement of the molybdenum atoms in the structure are all crystallographically equivalent and corresponds to the description of the compound as a molybdenum(V) oxide phosphate. From this point of view the diamagnetism observed for a molybdenum oxide phosphate glass, obtained by heat-treatment of crystalline MoOPO_4 at 950°C is quite interesting. The oxidation state of molybdenum in the glass is higher than in the crystalline starting material, but still considerably below the maximum oxidation state of the metal. An interpretation of this observation in terms of structure seems premature. Further work is contemplated in order to shed light on this problem.

5. SOME GENERAL ASPECTS AND PLANS FOR FURTHER RESEARCH

The studies on structural relations in crystalline and vitreous compounds which have been conducted at this Institute for a three-year period and are described above and also in two previous annual reports, have turned out to hit on a very interesting and profitable field of research. It is felt that the results arrived at have contributed to the understanding of the structural relations which have formed the goal of the research. The work has also raised an interest in several new problems relevant to this field of research. In some cases supplementary experimental and theoretical work will be required to make it possible to extract full information from the material and results now available. This would also provide an improved basis for a general comprehensive discussion of the complex of problems included within the wide range of the present research.

The present research program has comprised studies on the structural relations in the crystalline and vitreous states for various groups of compounds. An extension of this research, which now presents itself as an urgent one is to include also the molten state. Comparative investigations, using X-ray diffraction techniques and also other methods, of the atomic arrangements present in crystals, melts and glasses of suitable compounds are likely to be a very profitable field of research. Such studies should include investigations of melts and glasses over series of temperatures. Due consideration should also be given to the premelting region of the crystalline materials. The materials to be studied should be selected very carefully to meet the requirements to suit the experimental techniques and also to possess such a moderate structural complexity as to allow atomic rearrangements in the various states of aggregation.

Research along the lines described above are now being contemplated at this Institute.

ACKNOWLEDGEMENTS

The authors wish to thank Professor Arne Magnéli, Head of this Institute, for his kindness in allowing them to perform this investigation at the Laboratory and for many stimulating discussions and invaluable advice in connection with this work.

Skilful and efficient cooperation has been rendered in the experimental work by Mr. Ove Alderbäck, Mr. Karl-Erik Johansson, Mr. Georg Kruuse, Mr. Herbert Larsson and Mrs. Stina Nord.

Thanks are due to Dr. Sven Westman for his correction of the English of this report.

The invaluable help of Mrs. Ruth Wilhelmi, who typed the manuscript, is gratefully acknowledged.

REFERENCES

- (1) P. Kierkegaard, K. Eistrat, K. Gustafsson, K.-E. Johansson and A. Skancke: Structural Studies on Vitreous Compounds. Final Technical Report, April 1966 DA-91-591-EUC-3635.
- (2) P. Kierkegaard, S. Axrup, B. Linnros, M. Nygren, M. Seleborg, K. Eistrat and M. Sundbäck: Studies on Structural Relations in Crystalline and Vitreous Compounds. Final Technical Report, March 1967 DA-91-591-EUC-3980.
- (3) L.P. Shoemaker, editor: World List of Crystallographic Computer Programs, 2nd Ed. International Union of Crystallography Commission on Crystallographic Computing. 1966.
- (3a) T.C. Furnas, Jr.: Single Crystal Orienter Instruction Manual. Direction 12130 A (1957). X-ray Department, General Electric, Milwaukee, Wisconsin.
- (4) P. Kierkegaard: Contributions to the Structural Chemistry of Organic and Biochemical Molecules I. Progress report 1/7 1966 - 31/12 1967. Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm Va.
- (5) P. Debye: Dispersion of Röntgen Rays. Ann. Physik 46 (1915) 809.
- (6) F. Zernike and J.A. Prins: The Bonding of X-Rays in Liquids as an effect of molecular arrangement. Z. Phys. 41 (1927) 184.
- (7) C. Finbak: The Structure of Liquids. Acta Chem. Scand. 3 (1949) 1279.
- (8) C.N.J. Wagner, H. Ocken, and M.L. Joshi: Interference and Radial Distribution Functions of Liquid Copper, Silver, Tin and Mercury. Z. Naturforschung 20 (1965) 325.
- (9) G. Johansson: private communication.
- (9a) N. Norman: Cylindrically Symmetrical Distribution Functions and their Application in the Structure Investigation of Cellulose. Acta Cryst. 7 (1954) 462.
- (9b) J. Krogh-Moe: A Method for Converting Experimental X-ray Intensities to an Absolute Scale. Acta Cryst. 9 (1956) 951.
- (9c) N. Norman: The Fourier Transform Method for Normalizing Intensities. Acta Cryst. 10 (1957) 370.

- (10) R.J.H. Gelsing, H.N. Stein and J.M. Stevels: Vitreous Alkali Tungstates. Phys. and Chem. of Glasses 7 (1966) 185.
- (11) M. Seleborg: A Refinement of the Crystal Structure of Disodium Dimolybdate. Acta Chem. Scand. 21 (1967) 499-504.
- (12) F. Hoermann: Contribution to the Knowledge of Molybdates and Wolframates. Z. anorg. u. allgem. Chem. 177 (1928) 145.
- (12b) I. Lindqvist: Some New Aspects of the Polymolybdates. Nova Acta Regiae Soc. Sci. Upsaliensis 4, 15 (1950) No. 1.
- (13) I. Lindqvist: Crystal Structure Studies on Anhydrous Sodium Molybdates and Tungstates. Acta Chem. Scand. 4 (1950) 1066.
- (14) P.T. Sarjeant and R. Roy: New Glassy and Polymorphic Oxide Phases Using Rapid Quenching Techniques. J. Amer. Cer. Soc. 50 (1967) 500.
- (15) R.J.H. Gelsing, H.N. Stein and J.M. Stevels: The Phase Diagram $K_2WO_4-WO_3$. Rec. des Travaux Chim. des Pays-Bas T.84, No. 9/10 (1965) 1452.
- (16) P. Caillet: Polymolybdates et polytungstates de sodium ou de potassium anhydres. Bull. Soc. Chim. France 12 (1967) 4750-4755.
- (17) M. Seleborg: The Crystal Structure of Dipotassium Trimolybdate. Acta Chem. Scand. 20 (1966) 2195-2201.
- (18) A. Magnéli: Studies on the Hexagonal Tungsten Bronzes of Potassium, Rubidium, and Caesium. Acta Chem. Scand. 7 (1953) 315-324.
- (19) J. Graham and A.D. Wadsley: A Crystallographic Examination of Tungsten Trioxide Whiskers. Acta Cryst. 14 (1961) 379-383.
- (20) A. Magnéli: Crystal structure studies on γ -tungsten oxide. Arkiv Kemi 1 (1949) 223-230.
- (21) V.I. Spitsyn and I.M. Kuleshov: The Binary System $Rb_2WO_4-WO_3$. Zhur. Fiz. Khim. 24 (1950) 1197-1200.
- (22) P. Kierkegaard: The Crystal Structure of $NaWO_2PO_4$ and $NaMoO_2PO_4$. Arkiv Kemi 18 (1962) 553.
- (23) P. Kierkegaard and S. Holmén: The Crystal Structure of $AgMoO_2PO_4$. Arkiv Kemi 23 (1964) 213.
- (24) G.R. Levi and G. Peyronel: Crystal Structure of the isomorphous group MP_2O_7 ($M = Si^{4+}, Ti^{4+}, Zr^{4+}, Sn^{4+}, Hf^{4+}$). Z. Krist. 92 (1935) 190.

- (25) G. Peyronel: Structure of UP_2O_7 . Z. Krist. 94 (1936) 311.
- (26) M. Sljukić, B. Matković and B. Prodić: Preparation and Crystallographic Data of Phosphates with Common Formula $M^I M^{IV}_2(PO_4)_3$ ($M^I = Li, Na, K, Rb, Cs$; $M^{IV} = Zr, Hf$). Croat. Chem. Acta 39 (1967) 145.
- (27) A. Colani: Research on Uranium Compounds. Ann. Chim. Phys. 12 (1907) 59.
- (28) A. Burdese and M.L. Borlera: The System between Anhydrous Phosphoric Acid and the Dioxides of Uranium and Thorium. Ann. Chim. 53 (1963) 344.
- (29) R.M. Douglas: Crystallographic Data for Orthorhombic Uranium(IV)-metaphosphate and Plutonium(IV)metaphosphate. Acta Cryst. 15 (1962) 505.
- (30) Y. Baskin: Preparation and Properties of Uranium Metaphosphate, $U(PO_3)_4$. J. inorg. nucl. Chem. 29 (1967) 383.
- (31) J.A. Victoreen: The Calculation of X-Ray Mass Absorption Coefficients. J. appl. Physics 20 (1949) 1141.
- (32) H.A. Eick and L. Kihlberg: The Crystal Structure of $VOMoO_4$. Acta Chem. Scand. 20 (1966) 722.
- (33) H.A. Eick and L. Kihlberg: The Crystal Structure of V_2MoO_8 . Acta Chem. Scand. 20 (1966) 1658.
- (34) L. Kihlberg: The Crystal Structure of $(Mo_{0.3}V_{0.7})_2O_5$ of $R-Nb_2O_5$ Type and a Comparison with the Structures of V_2O_5 and V_2MoO_8 . Acta Chem. Scand. 21 (1967) 2495.
- (35) L. Kihlberg: Crystal Structure Studies on Mo_5O_{14} , a Compound Exhibiting Two-Dimensional Disorder. Arkiv Kemi 21 (1963) 427.
- (36) R. Gruehn: A New Modification of Niobiumpentoxide. J. Less-Common Metals 11 (1966) 119.
- (37) S. Andersson: The Crystal Structure of Nb_3O_7F . Acta Chem. Scand. 18 (1964) 2339.
- (38) W. Freundlich: New Ternary Phases in the System Wolfram-Vanadium-Oxygen. Compt. Rend. 260 (1965) 3077.
- (39) P. Kierkegaard and M. Westerlund: The Crystal Structure of $MoPO_4$. Acta Chem. Scand. 18 (1964) 2217.

BLANK PAGE

Tunnel Structure of $K_2W_4O_{13}$

MADELEINE SELEBORG

Institute of Inorganic and Physical Chemistry, University of Stockholm,
Stockholm, Sweden

The existence of a phase $K_2W_4O_{13}$ was pointed out by Hoermann¹ and later confirmed by Gelsing *et al.*² For the present investigation this compound was prepared by heating an intimate mixture of wolfram trioxide and a surplus of potassium wolframate at 750°C in a platinum crucible. The crystals obtained were of a faintly greenish tinge and in the shape of long, extremely thin needles adhering very strongly to each other. The Guinier powder photograph agrees well with powder data of $K_2W_4O_{13}$ as given by Gelsing *et al.*²

The present structure was derived from three-dimensional Weissenberg data using $CuK\alpha$ radiation. The 434 independent reflections were estimated visually. No attempt to correct for absorption effects has been made as yet. The results are as follows:

$K_2W_4O_{13}$, hexagonal, $a = 15.530 \pm 0.003$, $c = 3.8502 \pm 0.0007$ Å,
 $z = 3$.

Space-group: $P6$ (No. 168).

The structure was derived from a Patterson synthesis and refined by least squares techniques to a present R -factor of 0.134. Only observed intensities were included in the refinement.

The structure is built up by WO_6 octahedra which by shared corners form six-membered rings. Through the centres of these rings are formed tunnels of infinite extension running in the direction of the short axis. This is a structural feature which several wolfram compounds have in common. The hexagonal wolfram bronzes³, which are represented by a potassium bronze and also by rubidium and caesium bronzes have tunnel structures. In these compounds the tunnels enclose

the statistically distributed alkali ions. The pseudo-hexagonal wolfram trioxide⁴, which has a superlattice due to the substitution of one molybdenum for every twelfth wolfram, contains six-edged empty channels running parallel to the *c*-axis which in this case is 3.834 Å. Empty tunnels of infinite extension are also found in the wolfram oxide $W_{18}O_{49}$ ⁵.

In the tetrwolframate the six potassium ions are probably placed in a six-fold position, thus occupying interstices of a somewhat complicated shape. The one-fold position OOz would also be a plausible site in analogy to the conditions in the wolfram bronzes. That this in fact may be the case is indicated by the difference Fourier syntheses and consequently by least squares refinements based on that assumption. The five remaining potassium ions would then be statistically distributed over the six-fold position. That the two types of tunnel interstices arise in the tetrwolframate, only one of which is present in the structurally similar wolfram bronzes is due to the coupling of the WO_6 octahedra in the two structures. While in the latter structure the six-membered rings are sharing octahedra with adjacent rings, in the tetrwolframate the rings which here may be regarded as "double", have no octahedra in common. They are more loosely connected sideways through shared corners, thus forming additional tunnels of a more irregular shape in between them.

The author wishes to thank Professor Arne Magnéli for his encouraging interest in this investigation which was started at his suggestion.

It has been sponsored in part by the Swedish Natural Science Research Council, and in part by the European Research Office, United States Army, Frankfurt am Main, Germany.

- ¹ F. Hoermann, Z. anorg. u. allgem. Chem., 1928, 177, 145.
- ² R.J.H. Gelsing, H.N. Stein and J.M. Stevels, Rec. des Trav. Chim. Pays-Bas, 1965, T.84, No. 9/10, 1452.
- ³ A. Magnéli, Acta Chem. Scand., 1953, 7, 315.
- ⁴ J. Graham and A.D. Wadsley, Acta Cryst., 1961, 14, 379.
- ⁵ A. Magnéli, Arkiv Kemi, 1949, 1, 223.

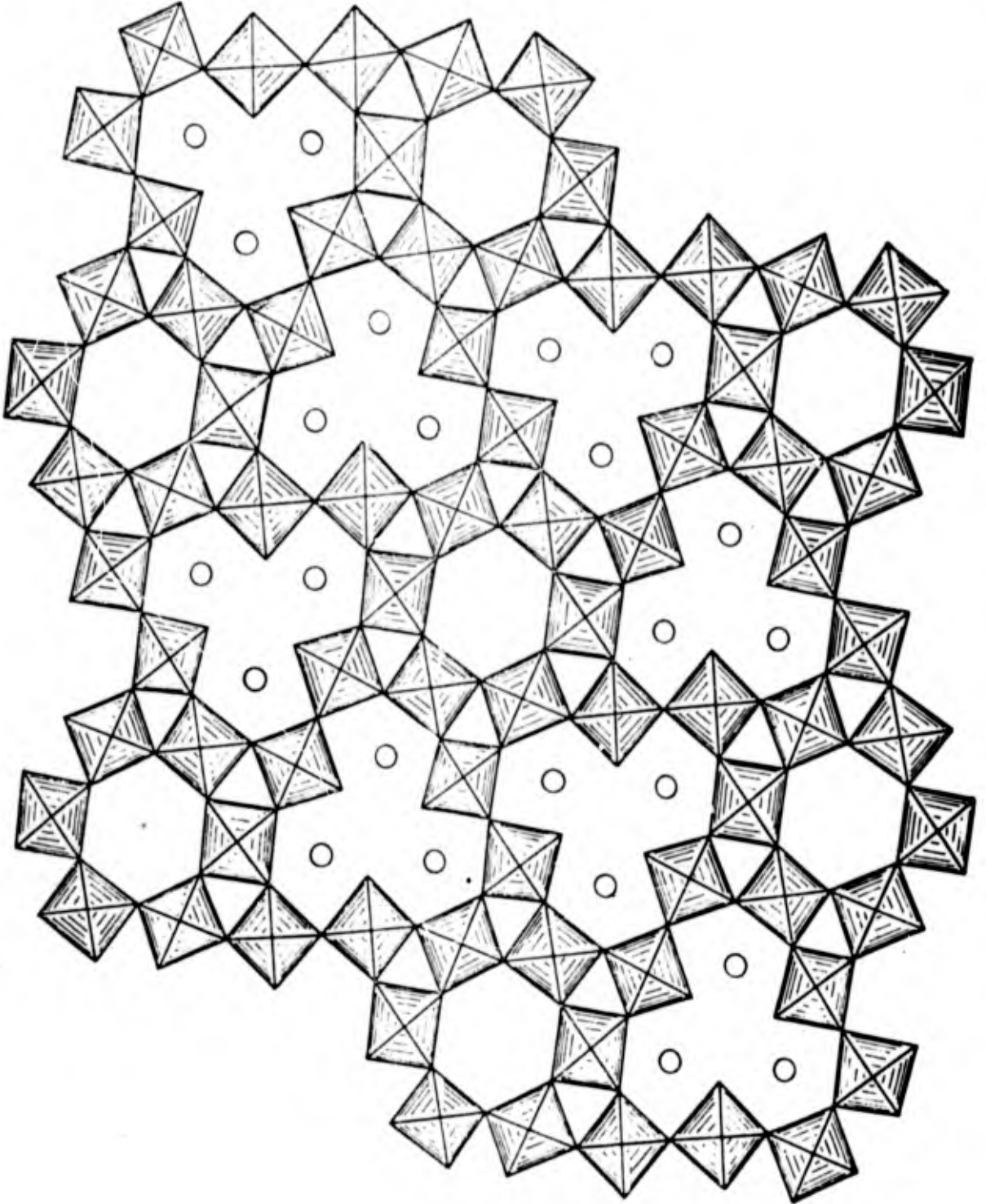


Fig. 1. The structure of K_2FeO_4 projected along $[001]$. The potassium ions in the six-fold position are drawn as circles.

Derivation of the Radial Distribution Function for Crystalline Materials from X-Ray Powder Data

PER-ERIK WERNER

In order to show the approximations and discuss the reliability of the radial distribution function applied to crystal powder data, this function is derived here and discussed in somewhat greater detail than is usual in the literature.

Consider a crystal powder containing N_0 atoms, having every possible orientation, scattering monochromatic X-rays. Assume there is only one kind of atom. Later the equations will be extended to cover the more general case.

According to Debye the coherent radiation

$$(1) \quad I = I_e \cdot f^2 \cdot \sum_{p=1}^{N_0} \sum_{q=1}^{N_0} \frac{\sin(kr_{pq})}{kr_{pq}} \quad \text{where } k = \frac{4\pi \sin\theta}{\lambda}$$

f is the atomic scattering factor and r_{pq} is the magnitude of the vector separating the atoms p and q .

$$I_e = I_0 \frac{e^4}{R^2 m^2 c^4} \cdot \frac{(1 + \cos^2\theta)}{2}$$

is the X-ray intensity from a Thomson electron if I_0 is the intensity of the unpolarized primary beam. R is the distance between the electron and the observation point (the camera radius). It is presupposed that r and λ are of the same order of magnitude and are both small compared to R .

Introduce a spherically symmetrical function $g(r)$, such that $4\pi r^2 g(r) dr$ atoms lie in a spherical shell at distances between r and $r+dr$ from the centre of an arbitrary atom.

$$(2) \quad I = I_e f^2 N_0 \left[1 + \int_0^\infty 4\pi r^2 g(r) \frac{\sin(kr)}{kr} dr \right] \quad (p=q)$$

In order to achieve convergence it is assumed that at large r

$$4\pi r^2 g(r) \rightarrow 4\pi r^2 g_0(r)$$

where $g_0(r)$ is the average atom density.

Expression (2) can be transformed to

$$(3) \quad I = I_e \cdot f^2 \cdot N_0 \left[1 + \int_0^\infty 4\pi r^2 [g(r) - g_0(r)] \frac{\sin(kr)}{kr} dr + \int_0^\infty 4\pi r^2 g_0(r) \frac{\sin(kr)}{kr} dr \right]$$

The second integral gives the radiation from the sample if the atoms were randomly spread out. For every k, big enough to be measured, this integral may be neglected. Therefore eq(3) may be rewritten.

$$(4) \quad k \left[\frac{I}{I_e N_0 f^2} - 1 \right] = \int_0^\infty 4\pi r [g(r) - g_0(r)] \sin(kr) dr$$

The Fourier integral theorem written in general form

$$f(x) = \frac{2}{\pi} \int_0^\infty \sin(xy) dy \int_0^\infty f(t) \sin(yt) dt$$

may be used in the following way. Put $x = t = r$ and $y = k$, then

$$f(r) = \frac{2}{\pi} \int_0^\infty \sin(kr) dk \int_0^\infty f(r) \sin(kr) dr$$

Introduce $h(k) = \int_0^\infty f(r) \sin(kr) dr$ I.e.

$$f(r) = \frac{2}{\pi} \int_0^\infty h(k) \sin(kr) dk$$

Put $h(k) = k \left[\frac{I}{I_e N_0 f^2} - 1 \right]$ and $f(r) = 4\pi r [g(r) - g_0(r)]$

Eq(4) can now be transformed to

$$(5) \quad 4\pi r [g(r) - g_0(r)] = \frac{2}{\pi} \int_0^{\infty} k \left[\frac{I}{I_e N_0 f^2} - 1 \right] \sin(kr) dk$$

or

$$(6) \quad 4\pi r^2 [g(r) - g_0(r)] = \frac{2r}{\pi} \int_0^{\infty} k \left[\frac{I}{I_e N_0 f^2} - 1 \right] \sin(kr) dk$$

The intensity I is composed of two parts

$$I = I_p + I_t$$

where I_p = the peak intensity

and $I_t = I_e N_0 f^2 \left[1 + e^{-Bk^2} \right]$ is the diffuse temperature scattering.

Therefore eq (6) can be written as

$$(7) \quad 4\pi r^2 [g(r) - g_0(r)] = \frac{2r}{\pi} \int_0^{\infty} \frac{k I_p}{I_e N_0 f^2} \sin(kr) dk - \frac{2r}{\pi} \int_0^{\infty} k e^{-Bk^2} \sin(kr) dk$$

The second integral may be solved in the following way

$$\begin{aligned} \int_0^{\infty} \underbrace{\sin(kr)}_v \cdot \underbrace{k e^{-Bk^2}}_u dk &= \int_0^{\infty} \underbrace{\sin(kr)}_v \cdot \underbrace{\frac{e^{-Bk^2}}{-2B}}_u dk \\ &= \int_0^{\infty} \frac{e^{-Bk^2}}{-2B} \frac{r \cos(kr)}{v} dk = \frac{r}{2B} \int_0^{\infty} e^{-Bk^2} \frac{(e^{1kr} - e^{-1kr})}{2} dk = \\ &= \frac{r}{4B} \int_0^{\infty} e^{-(\sqrt{B}k - \frac{1r}{2\sqrt{B}})^2 - \frac{r^2}{4B}} \cdot \frac{d(\sqrt{B}k - \frac{1r}{2\sqrt{B}})}{\sqrt{B}} + \end{aligned}$$

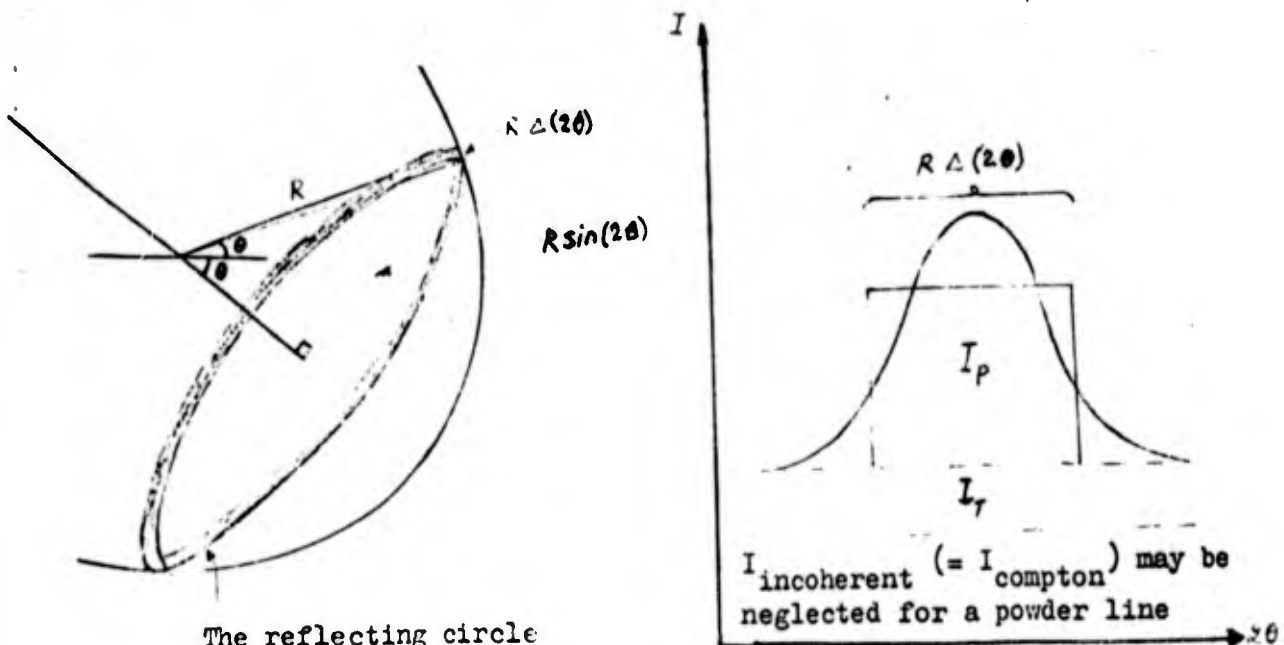
$$\begin{aligned}
 & + \frac{r}{4B} \int_0^{\infty} e^{-\left(\sqrt{B}k + \frac{ir}{2\sqrt{B}}\right)^2} - \frac{r^2}{4B} \cdot \frac{d\left(\sqrt{B}k + \frac{ir}{2\sqrt{B}}\right)}{\sqrt{B}} = \\
 & = \frac{r}{2B^{3/2}} \cdot e^{-\frac{r^2}{4B}} \int_0^{\infty} \frac{e^{-x^2}}{\frac{\sqrt{\pi}}{2}} dx = \frac{r\sqrt{\pi}}{4B^{3/2}} \cdot e^{-\frac{r^2}{4B}}
 \end{aligned}$$

(Ch.-J. de La Vallée Poussin, Cours d'Analyse Infinitésimale, I. p. 239, Guathier-Villars, Paris 1954.)

As can be seen this value decreases strongly with increasing r. For not too small r-values the second integral in eq (7) may be neglected. I.e.

$$(8) \quad r[g(r) - g_0(r)] = \frac{1}{2\pi^2} \int_0^{\infty} \frac{kI_p}{I_e N_o f^2} \sin(kr) dk$$

The total intensity P in a powder diffraction line is $I_p \cdot \Delta A$ where ΔA is the area of the complete reflecting circle.



The reflecting circle
 The circumference = $2\pi R \sin(2\theta)$

From this follows

$$(9) \quad P = I_P \cdot \Delta A = I_P \cdot 2\pi R \sin(2\theta) \cdot R \Delta (2\theta)$$

$$dk = \frac{2\pi \cos \theta}{\lambda} d(2\theta), \quad kdk = \frac{4\pi^2}{\lambda^2} \sin(2\theta) d(2\theta)$$

which, introduced into eq (9), gives

$$(10) \quad P = I_P \frac{R^2 \lambda^2}{2\pi} k \Delta k$$

Eq (8) can now be written

$$(11) \quad r[g(r) - g_0(r)] = \frac{1}{\pi} \sum_0^{\infty} \frac{P \sin(kr)}{I_e N_0 f_R^2 \lambda^2}$$

If more than one kind of atom is present it is possible to introduce an approximation for the atomic scattering factors. Put

$$(12) \quad f_m = K_m \cdot f_e$$

where f_m is the atomic scattering factor for the m :th atom, K_m is the number of effective electrons in the atom and f_e is the electronic scattering factor for a Thomson electron. Eq (11) may then be transformed to

$$(13) \quad r[\rho(r) - \rho_0(r)] = \frac{1}{\pi} \sum_0^{\infty} \frac{P \sin(kr)}{I_e N_0 f_R^2 \lambda^2}$$

where $\rho(r)$ is the electron distribution function analogous to the function $g(r)$. (See above.)

For a powder ring

$$(14) \quad \frac{P}{I_0} = \frac{N^2 e^4 \lambda^3 V}{8\pi^2 c^4} \frac{[1 + \cos^2(2\theta)] \cdot p''}{\sin \theta} \cdot F^2$$

(Int. Tab. Vol. II, 314) and for an electron

$$(15) \quad \frac{I_e}{I_o} = \frac{e^4}{R^2 m^2 c^4} \frac{[1 + \cos^2(2\theta)]}{2}$$

(Int. Tab. Vol. II, 237)

Therefore eq (13) can be written

$$(16) \quad r[\rho(r) - \rho_o(r)] = \sum_0^{\infty} \frac{N \cdot p'' \cdot |F|^2 \sin(kr)}{u f^2 k}$$

where N is the number of unit cells per unit volume, p'' is the multiplicity factor, and u is the number of atoms per unit cell.

For a Guinier camera

$$(17) \quad PLG = \frac{1 + \cos^2(2\alpha) \cos(2\theta)}{[1 + \cos^2(2\alpha)] \sin \theta \sin(3\theta)}$$

if the angle between the Guinier camera and the primary beam is 30° .

P = the polarization factor

L = the Lorentz factor

G = the geometrical factor

$\alpha = 13^\circ 24'$ for a quartz monochromator

(K. Sagel, Tabellen zur Röntgenanalyse (1958) 78-79)

If the observed relative intensity in a powder line is denoted $I(\theta)$ and if the absorption factor $A(\theta)$ is equal to $\frac{1}{2\mu}$ or negligible, and a convergence factor $e^{-\frac{\beta \sin^2 \theta_1}{\lambda^2}}$ is introduced, it is possible to approximate eq (16) as

$$(18) \quad r[\rho(r) - \rho_o(r)] = K_1 \sum_{h=1}^n \frac{[1 + \cos^2(2\alpha)] \sin \theta_1 [3 - 4 \sin^2 \theta_1]}{1 + \cos^2(2\alpha) [1 - 2 \sin^2 \theta_1]} \cdot e^{-\frac{\beta \sin^2 \theta_1}{\lambda^2}} \cdot I(\theta_1) \cdot \sin \left[\frac{4\pi \sin \theta_1}{\lambda} \cdot r \right]$$

where K is an arbitrary scale factor. The radial distribution function is placed on an arbitrary scale.

For other camera techniques the PLG factors and therefore eq (18) must be changed. The PLG factors needed are easily found in Tabellen zur Röntgenanalyse (1958), K. Sagel.

The termination-of-series errors in the summation process may be illustrated with two periodic waves. The upper limit gives a wave of a short wavelength which can seriously affect the positions of the maxima if the intensities for high θ -values are not negligible. Therefore it is sometimes favourable to replace the Guinier camera by another camera. The radiation used should be of as short wavelength as possible.

The lower limit introduced does not seem to be very serious. It may be discussed as a long periodic wave which affects the amplitudes more than the positions of the maxima in the distribution function.

Programs for the radial distribution function eq (18) has been made for the computers CDC 3200 and IEM 1800.

BLANK PAGE

The crystal structure of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ of $\underline{\text{R-Nb}}_2\text{O}_5$ type and a
Comparison with the Structures of V_2O_5 and V_2MoO_8

LARS KIHNBORG

Institute of Inorganic and Physical Chemistry, University of Stockholm,
Stockholm, Sweden

ABSTRACT

$(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ represents the molybdenum rich limit (at 650°C) of a range of solid solution extending from V_2O_5 along the line $(\text{Mo}_x\text{V}_{1-x})_2\text{O}_5$ in the Mo-V-O system. There are, however, discontinuities within this range associated with symmetry changes. This phase has been studied by single crystal diffraction methods. The dimensions of the monoclinic unit cell are $a = 11.809 \text{ \AA}$, $b = 3.652 \text{ \AA}$, $c = 4.174 \text{ \AA}$, $\beta = 90.57^\circ$, and the space group is $\underline{\text{C2}}$.

The structure is of the same type as that of $\underline{\text{R-Nb}}_2\text{O}_5$ and can be considered as composed of $\underline{\text{MO}}_6$ octahedra coupled in the same way as in V_2O_5 , although the distortion of the metal atoms within the octahedra follows a different pattern. This distortion, as reflected in the considerable divergence of the $\underline{\text{M}} - \text{O}$ bond lengths, is intermediate in magnitude between that in V_2O_5 and MoO_3 . Molybdenum and vanadium atoms are randomly distributed over the metal atom positions.

The structure is also closely related to that of V_2MoO_8 .

In the course of an investigation of the phases formed in the system V-Mo-O¹ it has been observed that molybdenum may replace vanadium in V_2O_5 . This replacement gives rise to a range of solid solution, $(\text{Mo}_x\text{V}_{1-x})_2\text{O}_5$, extending at 650°C to the composition $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ approximately. To a first approximation the unit cell dimensions vary gradually within this interval but a closer examination of the powder

patterns and comparison with single crystal photographs revealed that the symmetry has changed from orthorhombic for V_2O_5 to monoclinic for $(Mo_{0.3}V_{0.7})_2O_5$. According to preliminary results, this transition occurs at a composition of about $x = 0.20$ and is probably associated with the occurrence at this composition of a phase giving a more complex powder pattern. Further studies of these problems are in progress.

This article presents a structure determination of a crystal with a composition close to the molybdenum-rich limit. A short communication of the investigations reported below was given at the Seventh International Congress of Crystallography².

EXPERIMENTAL

The crystal studied was selected from a sample prepared by heating a mixture of MoO_3 , V_2O_5 and V_2O_3 of gross composition $Mo_{0.3}V_{0.7}O_{2.5}$ in a sealed silica tube at $650^\circ C$ for 2 days. The powder pattern of this sample showed the lines (Table 1) of a phase which could be indexed on the basis of a monoclinic unit cell with the dimensions given in Table 2. A few additional weak lines could be assigned to VO_4^{3-} and it seems therefore probable that the monoclinic phase contained slightly less molybdenum than indicated by the gross composition and that its formula should be approximately $(Mo_{0.28}V_{0.72})_2O_5$.

The crystal was shaped like a somewhat truncated parallelepiped with the dimensions 0.0204 mm (along a), 0.0636 mm (along b), and 0.0053 mm (along c). Integrated Weissenberg photographs were recorded of the h0l, h1l and h2l layer lines using $CuK\alpha$ radiation and multiple film technique. The relative intensities of the reflections were measured by means of a densitometer. These values were corrected for the effect of absorption (crystal assumed to be bounded by 7 planes; $\mu = 496 \text{ cm}^{-1}$) and the usual I_p -correction was applied. These calculations as well as the subsequent structure factor calculations, least squares refinement and calculations of interatomic distances were performed on a computer of type FACIT EDB by means of the programs No.

6015, 6016, 6019, 6023 and 6030⁴ (the Lp-program written by B. Lundberg is not listed in Ref. 4). The atomic scattering factors listed in International Tables⁵ were used, namely, for neutral oxygen and vanadium the values given in Table 3.3.1 A and for molybdenum those given in Table 3.3.1 B. The real part of the dispersion correction⁵ was applied to these values.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

Systematic extinction was observed for all reflections hkl with $h+k = 2n+1$. Together with the observed Laue symmetry $2/m$ this led to the three possible space groups C2/m (No. 12), C2 (No. 5) and Cm (No. 8).

The fact that the crystal under investigation represented one end of a range of solid solution (cf. above) the other limit of which is V_2O_5 suggested a close relationship between the crystal structures. The space group of V_2O_5 is Pmm (No. 59)^{6,7} or possibly Pmn2₁ (No. 31)⁷ which, on the other hand, implies a basic difference between the two structures.

A model was tried in which the arrangement of MO_6 octahedra was the same as in V_2O_5 but in which the distortion of the metal atoms from the centres of these octahedra was different to account for the different symmetry. Structure factor calculations and least squares refinement proved this model to be correct. The structure is shown in Fig. 1 together with that of V_2O_5 . Completely random distribution of molybdenum and vanadium atoms over the metal atom positions had to be assumed since these positions were crystallographically equivalent and no indication of a superstructure had been observed on the X-ray photographs. Because of the uncertainty in the exact composition of the crystal (cf. above) three different Mo:V ratios were tested, viz. $M = (0.33 \text{ Mo} + 0.67 \text{ V})$, $(0.30 \text{ Mo} + 0.70 \text{ V})$, and $(0.27 \text{ Mo} + 0.73 \text{ V})$. The results, obtained by least squares refinement, differed only insignificantly however.

The space group \underline{Cm} was not consistent with the structure model but the remaining two, $\underline{C2/m}$ and $\underline{C2}$, were both possible. Least squares refinement was carried out for both alternatives, namely (I) 1 \underline{M} and 2 O in positions 4 \underline{i} , and 1 O in 2 \underline{a} of space group $\underline{C2/m}$ and (II) 1 \underline{M} and 2 O in 4 \underline{c} and 1 O in 2 \underline{a} of space group $\underline{C2}$. The final \underline{R} -values (based on observed reflections only) were about the same for both alternatives, viz. 0.071 and 0.070, respectively, but the final \underline{y} coordinates of O(1) and O(2) in alternative II differed by 7.4 σ and 5.1 σ , respectively (σ = the corresponding standard deviation) from the values 0 and $\frac{1}{2}$ at which they are fixed by symmetry in alternative I. The temperature factors obtained were also less divergent in alt. II than in alt. I and, particularly, they were much lower for atoms O(1) and O(2) in alt. II. It was thus evident that the structure is best described in the non-centrosymmetric space group $\underline{C2}$ and the final parameters for this case are given in Table 2.

Weights in the least squares procedure were calculated according to Cruickshank's formula, $\underline{w} = 1/(\underline{A} + \underline{F}_0 + \underline{C} \cdot \underline{F}_0^2)$, where the following values were chosen for the parameters, $\underline{A} = 18$, $\underline{C} = 0.012$. The final weight analysis is given in Table 3. The observed and calculated structure factors are listed in Table 4.

DISCUSSION

The structure of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ turns out to be isotypic with that recently suggested by Gruehn for $\underline{R}\text{-Nb}_2\text{O}_5$ on the basis of powder diffraction data⁶. The unit cell dimensions given for $\underline{R}\text{-Nb}_2\text{O}_5$ are (the \underline{a} and \underline{c} axes interchanged here), $\underline{a} = 12.7_9 \text{ \AA}$, $\underline{b} = 3.82_6 \text{ \AA}$, $\underline{c} = 3.98_3 \text{ \AA}$, $\beta = 90.7_5^\circ$. The space group was assumed to be ($\underline{A2/m} =$) $\underline{C2/m}$ and the following atomic coordinates were reported (the numbering of the atoms changed here to become analogous with that in Table 2).

	\underline{x}	\underline{y}	\underline{z}
Nb	0.146	0	0.07
O(1)	0.16	0	0.5
O(2)	0.18	0.5	0
O(3)	0	0	0

A comparison with Table 2 emphasizes the similarity between the two structures. The discussion below, therefore, applies also to $\underline{R}\text{-Nb}_2\text{O}_5$.

The coordination of oxygen atoms around vanadium in V_2O_5 may be described either as five- or sixfold since the sixth V-O bond is considerably longer than the other five^{7,8}. If the coordination is regarded as six-fold the structure may be described as built up of octahedra sharing edges and corners as visualized in Fig. 1b. Comparison with Fig. 1a indicates that the coupling of the octahedra is the same in $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$. The structures can thus be described as built of edge sharing octahedra which form zig-zag chains that run in the \underline{b} direction. These chains are mutually connected by corner sharing between octahedra in adjacent chains. Alternatively, they may be regarded as consisting of slabs of ReO_3 -type, two octahedra thick, which extend infinitely in the \underline{bc} plane; these, in turn, are interconnected by edge-sharing between component octahedra. The latter is a description in terms of a shear structure⁹ introduced by Magnéli¹⁰ and later developed by Andersson¹¹.

The difference between the two structures becomes significant when the distortions of the metal atoms from the centres of the octahedra are considered. These displacements occur predominantly along the direction of the \underline{c} axis. It is seen in Fig. 1 that in V_2O_5 all metal atoms within an ReO_3 -type slab are displaced in the same direction while in $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ they are shifted pairwise in opposite directions. The reason for this interesting difference between the two structures is not understood and is being further investigated. In both structures the metal atoms in a pair of octahedra sharing edges are displaced in opposite directions which, of course, is energetically most favourable from a purely electrostatic point of view.

It is interesting to compare these two structures with that of V_2MoO_8 ¹² shown in Fig. 2. Here the slabs of ReO_3 type have a thickness of three octahedra instead of two but the interconnection

of the slabs remains the same. Homologous series of structures is a term introduced by Magnéli for this type of structural relationship¹⁰. Considering the off-center displacements of the metal atoms V_2MoO_8 forms an intermediate between the above mentioned structures since the displacement within the middle octahedra of each slab goes in both directions; it alternates between $+z$ and $-z$ when going in the direction of the b axis which is therefore doubled (cf. Fig. 2). Both types of relative displacement within neighbouring octahedra are thus present simultaneously in this structure.

The $M-O$ distances which are given in Table 5 can be grouped together in three short, two intermediate and one long bond. There is thus a marked tendency towards five-fold coordination although not as pronounced as in V_2O_5 . The range of the $M-O$ distances is seen to be intermediate between those in V_2O_5 and MoO_3 . All close O-O distances have normal values ranging from 2.48 (± 6) Å (along the shared edge) to 2.97 (± 2) Å. The Nb-O distances in $R-Nb_2O_5$ as given by Gruehn⁶ range from 1.7 to 2.3 Å which indicates a slightly smaller distortion in that structure than in the isostructural $(Mo_{0.3}V_{0.7})_2O_5$.

* * *

The work reported in this article forms a part of a research program sponsored in part by the Swedish Natural Science Research Council and in part by the European Research Office, United States Army, Frankfurt am Main, Germany. Grants for the use of computers were received from the Computer Division of the National Swedish Rationalization Agency (Kungl. Statskontoret).

I am indebted to Professor A. Magnéli for valuable comments on the manuscript.

REFERENCES

1. Kihlborg, L. To be published.
2. Kihlborg, L. and Eick, H.A. *Acta Cryst.* 21 (1966) A 59.
3. Eick, H.A. and Kihlborg, L. *Acta Chem. Scand.* 20 (1966) 722.
4. IUCr World List of Crystallographic Computer Programs, 2nd ed. A. Oosthoek's Uitgevers Mij. N.V., Utrecht 1966.
5. International Tables for X-ray Crystallography, Vol. III, The Kynoch Press, Birmingham 1962.
6. Gruehn, R. *J. Less-Common Metals* 11 (1966) 119.
7. Byström, A., Wilhelmi, K.-A. and Brotzen, O. *Acta Chem. Scand.* 4 (1950) 1119.
8. Bachmann, H.G., Ahmed, F.R. and Barnes, W.H. *Z. Krist.* 115 (1961) 110.
9. Wadsley, A.D. *Revs. Pure and Appl. Chem. (Australia)* 5 (1955) 165.
10. Magnéli, A. *Acta Cryst.* 6 (1953) 495.
11. Anderson, S. *Bull. Soc. Chim. France* 1965, 1088.
12. Eick, H.A. and Kihlborg, L. *Acta Chem. Scand.* 20 (1966) 1658.
13. Hambling, P.G. *Acta Cryst.* 6 (1953) 98.
14. Kihlborg, L. *Arkiv Kemi* 21 (1963) 357.

Table 1. X-ray powder diffraction data for $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$,
 $\text{CuK}\alpha$ radiation. ($\lambda = 1.54051 \text{ \AA}$)

<u>I</u>	$\frac{d_{\text{obs}}}{\text{\AA}}$	$\sin^2 \theta_{\text{obs}}$ $\times 10^5$	<u>hkl</u>	$(\sin^2 \theta_{\text{obs}} - \sin^2 \theta_{\text{calc}})$ $\times 10^5$
w	5.894	1708	200	+ 6
w+	4 169	3414	001	+ 9
st	3.487	4878	110	+ 5
w	3.419	5074	$\bar{2}01$	+14
w	3.392	5157	201	+ 2
w+	2.952	6810	400	+ 3
st	2.678	8270	$\left\{ \begin{array}{l} 111 \\ 310 \\ \bar{1}11 \end{array} \right.$	$\begin{array}{l} +32 \\ - 7 \\ -16 \end{array}$
vw	2.420	10131	$\bar{4}01$	+13
vw	2.087	13621	002	0
w	1.9685	15311	600	- 6
vw	1.9638	15384	202	-34
m	1.8270	17775	020	-15
w	1.7980	18353	$\bar{5}11$	-17
w	1.7944	18426	$\bar{1}12$	-20
vw	1.7458	19466	220	-26
vw	1.7117	20250	$\bar{4}02$	+12
w	1.6738	21178	021	-17
w	1.6086	22927	221	-18
w+	1.5533	24589	420	- 9
m	1.5316	25293	710	- 2
vw	1.4583	27898	$\bar{4}21$	-10
w	1.4583	28461	$\bar{5}12$	- 7
vw	1.4415	28551	$\bar{7}11$	+17

Table 1, cont.

m	1.3386	33110	620	+ 3
w	1.2722	36659	621	+ 4
vw	1.2541	37724	403	-15
vw	1.2488	38046	422	+17
vw	1.2109	40460	$\begin{cases} 802 \\ 130 \end{cases}$	$\begin{matrix} -11 \\ + 6 \end{matrix}$
vw	1.1809	42545	$\begin{cases} 911 \\ 10,0,0 \end{cases}$	$\begin{matrix} +17 \\ - 1 \end{matrix}$
w	1.1633	43841	$\begin{cases} 731 \\ 330 \end{cases}$	$\begin{matrix} + 6 \\ -16 \end{matrix}$
vw	1.1235	47000	622	-13
vw	1.1214	47175	331	-16
vw	1.1197	47325	331	- 9

Table 2. The crystal structure of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$.Space group: C_2 (No. 5)Unit cell dimensions *: $\underline{a} = 11.809$ (± 2) Å $\underline{b} = 3.652$ (± 1) Å $\underline{c} = 4.174$ (± 1) Å $\beta = 90.57$ (± 2) °Unit cell content: $2 \underline{M}_2\text{O}_5$, $\underline{M} = (\text{Mo}_{0.28}\text{V}_{0.72})$,
Mo/V ratio approximative (see text).

Atom Position		$\underline{x} \pm \sigma(\underline{x})$	$\underline{y} \pm \sigma(\underline{y})$	$\underline{z} \pm \sigma(\underline{z})$	$\underline{B} \pm \sigma(\underline{B})$
\underline{M}	$4c$	$.14892 \pm .00025$	0	$.10034 \pm .00076$	$0.441 \pm .038$
O(1)	$4c$	$.1446 \pm .0015$	$.0651 \pm .0088$	$.4934 \pm .0042$	$1.09 \pm .32$
O(2)	$4c$	$.1792 \pm .0013$	$.5518 \pm .0102$	$.9953 \pm .0037$	$0.51 \pm .26$
O(3)	$2a$	0	$.002 \pm .034$	0	$1.73 \pm .47$

* $\lambda[\text{CuK}\alpha_1] = 1.54051$ Å, $\underline{a}[\text{KCl}, 25^\circ\text{C}] = 6.29228$ Å¹³.

Table 3. Weight analysis obtained in the last cycle of refinement.

$$\Delta = \left| \frac{F_{\text{obs}}}{|F_{\text{obs}}|} - \frac{F_{\text{calc}}}{|F_{\text{calc}}|} \right|, \quad w = \text{weighting factor.}$$

The $w\Delta^2$ values have been normalized.

Interval sin θ	Number of independent reflections	$\overline{w\Delta^2}$	Interval $ F_{\text{obs}} $	Number of independent reflections	$\overline{w\Delta^2}$
0.00-0.46	26	0.71	0 - 16	3	0.47
0.46-0.58	21	0.84	16 - 24	7	1.75
0.58-0.67	15	1.49	24 - 32	29	1.19
0.67-0.74	15	0.82	32 - 40	32	1.11
0.74-0.79	13	0.51	40 - 48	19	1.04
0.79-0.84	11	1.20	48 - 56	18	0.60
0.84-0.89	10	0.99	56 - 64	14	0.86
0.89-0.93	7	1.28	64 - 72	7	0.76
0.93-0.97	15	0.82	> 72	10	0.73
0.97-1.00	6	2.94			

Table 5. Metal oxygen distances.

$(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$			V_2O_5 (8)	MoO_3 (14)
Atoms	Coordinates	Distance (in Å)	Distance (in Å)	Distance (in Å)
<u>M</u> -	.149 0 .100			
- O(1)	.145 .065 .493	1.659 ± 18	1.585	1.671
- O(2)	.179 -.448 -.005	1.733 ± 36	1.780	1.734
- O(3)	0 .002 0	1.804 ± 3	1.878	1.948
- O(2)	.321 .052 .005	2.081 ± 16	1.878	1.948
- O(2)	.179 .552 -.005	2.094 ± 36	2.021	2.251
- O(1)	.145 .065 -.507	2.544 ± 18	2.785	2.332

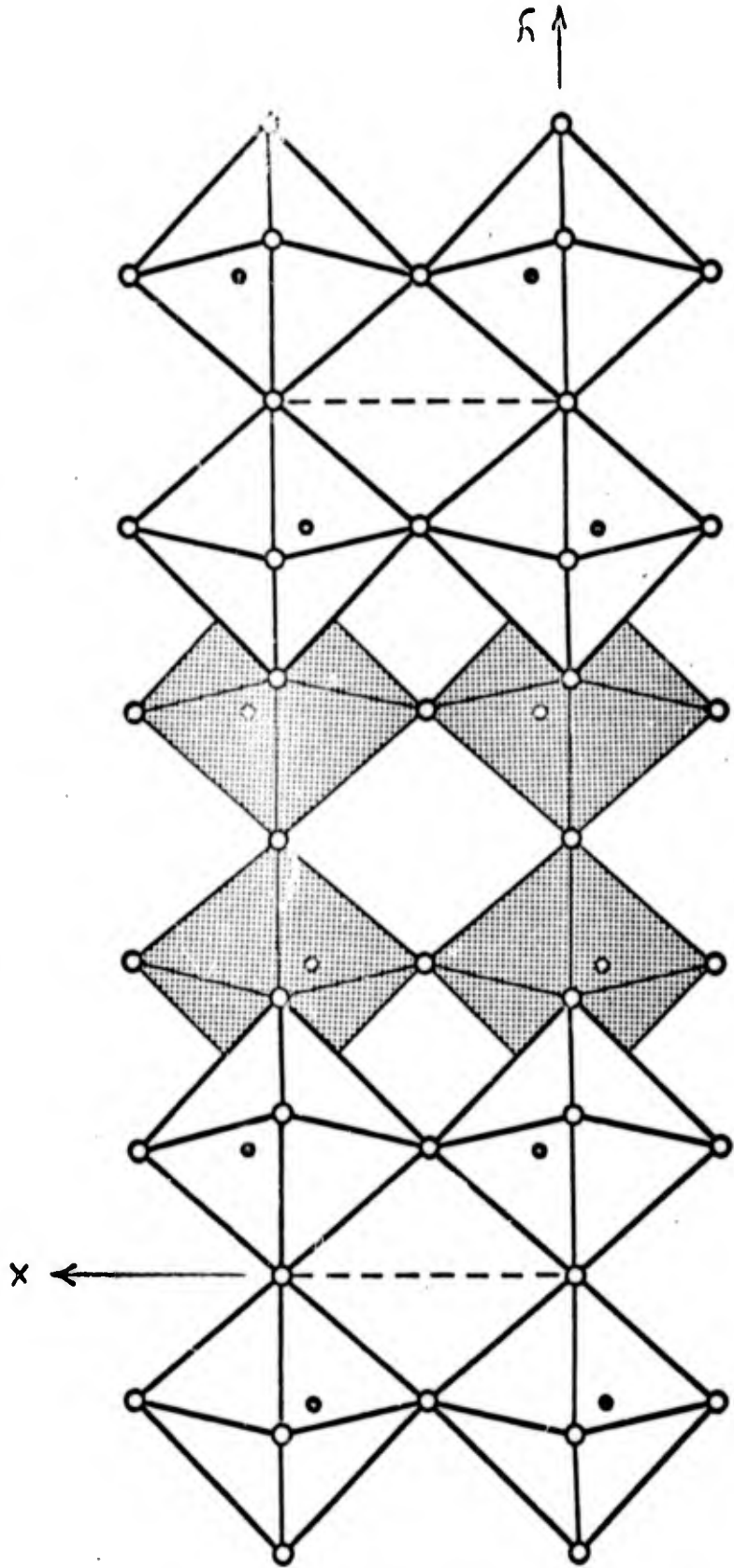


Fig. 1a. The structure of $(\text{Mo}_{0.3}\text{V}_{0.7})_2\text{O}_5$ visualized as built up of MO_6 octahedra at two levels (light and shaded, respectively). These polyhedra share corners with crystallographically identical ones above and below the positions of the metal atoms inside the octahedra are indicated by dots.

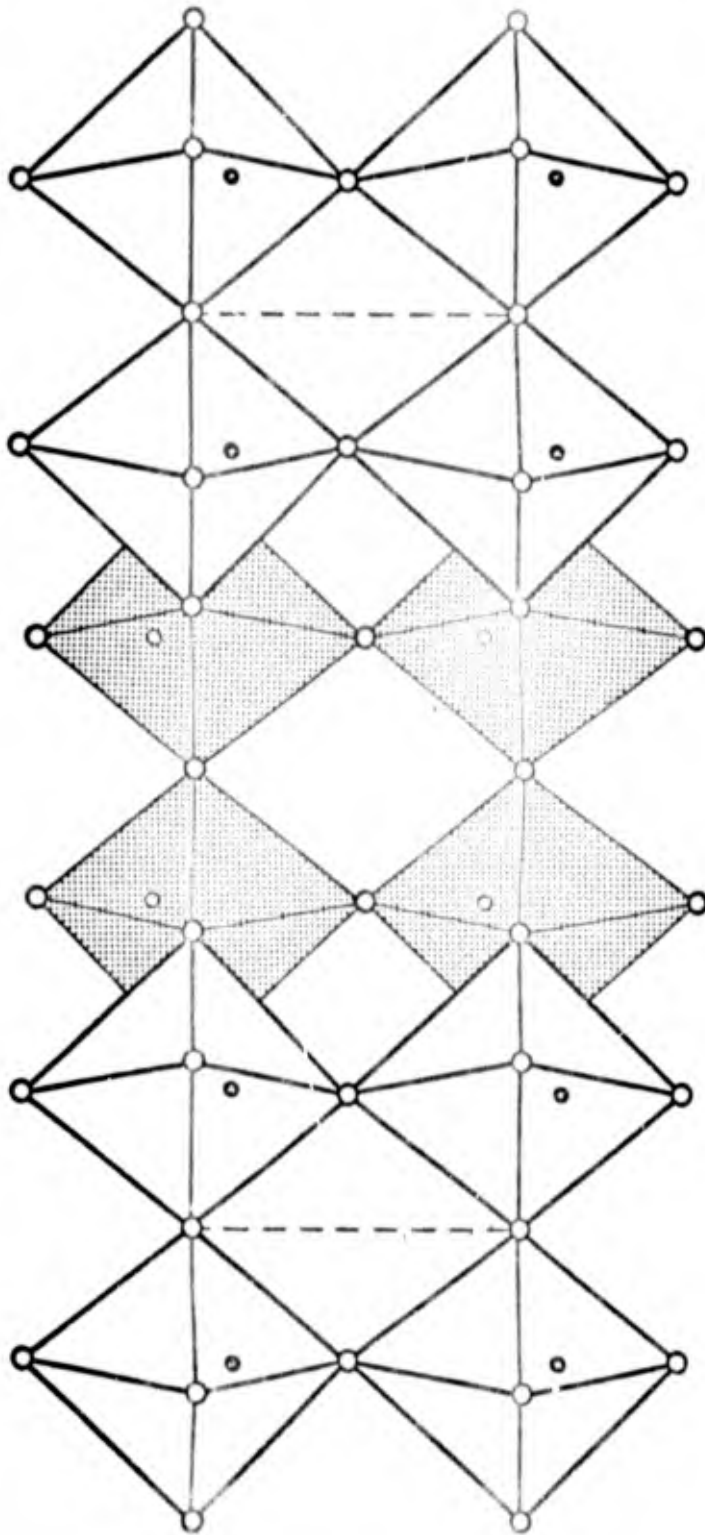


Fig. 1b. The structure of V_2O_5 visualized as built up of MO_6 octahedra at two levels (light and shaded, respectively). These polyhedra share corners with crystallographically identical ones above and below the positions of the metal atoms inside the octahedra are indicated by dots.

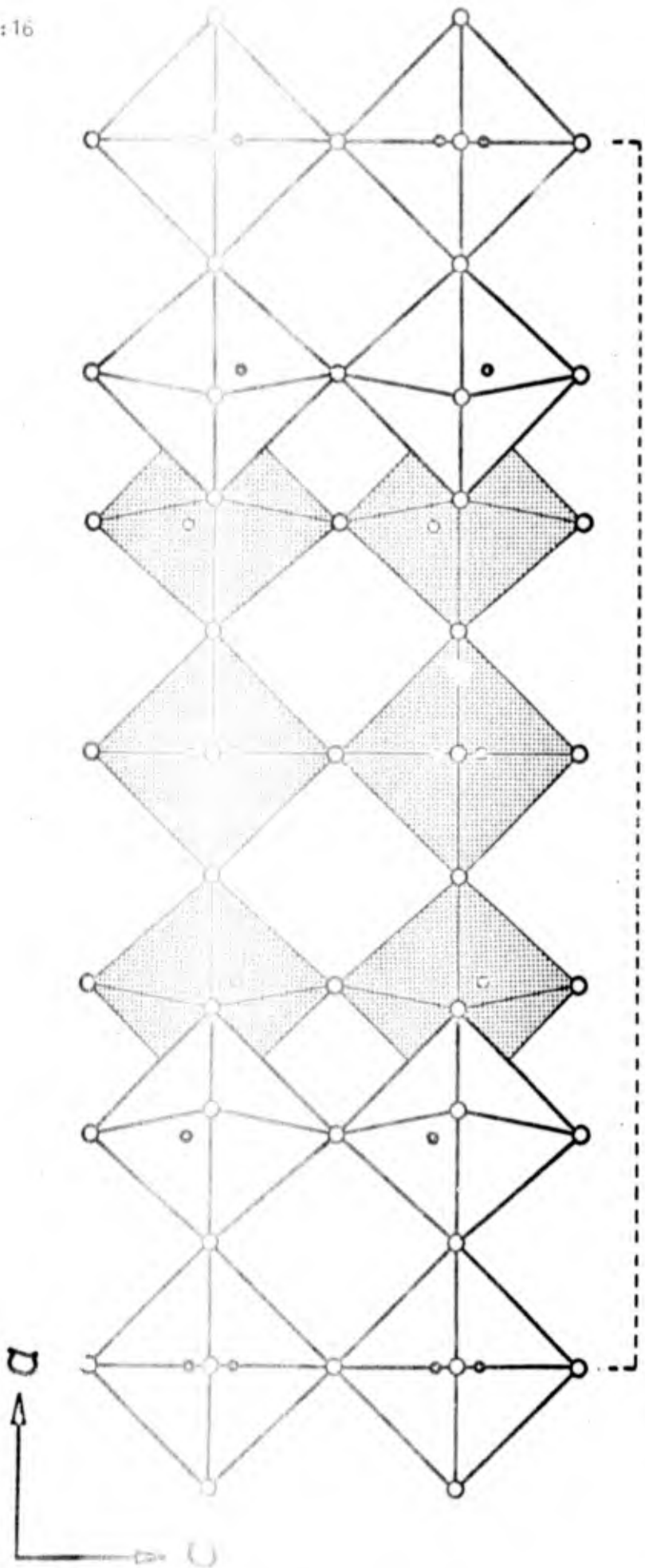


Fig. 2. The structure of V_2MoO_8 presented analogously with those in Fig. 1. In the octahedra containing two dots the metal atoms are situated alternately at the two positions in the strings of octahedra running along the line of sight. The dashed line indicates a repeat distance.

The Crystal Structure of $\text{NaMe}_2^{\text{IV}}(\text{PO}_4)_3$, $\text{Me}^{\text{IV}} = \text{Ge, Ti, Zr}$

LARS-OVE HAGMAN and PEDER KIERKEGAARD

Institute of Inorganic and Physical Chemistry, University of Stockholm,
Stockholm, Sweden

The crystal structure of $\text{NaZr}_2(\text{PO}_4)_3$, a representative of an extensive group of isomorphous mixed phosphates containing alkali metals and germanium, titanium, zirconium or hafnium, has been determined from three-dimensional X-ray data. The space group is $R\bar{3}/c$ and the dimensions of the hexagonal unit cell for the three members of the series studied by the present authors are

$$\begin{array}{lll} \text{NaZr}_2(\text{PO}_4)_3 & a = 8.8043 \pm 2 \text{ \AA} & c = 22.7585 \pm 9 \text{ \AA} \\ \text{NaTi}_2(\text{PO}_4)_3 & a = 8.4924 \pm 5 \text{ \AA} & c = 21.7788 \pm 15 \text{ \AA} \\ \text{NaGe}_2(\text{PO}_4)_3 & a = 8.1123 \pm 4 \text{ \AA} & c = 21.5133 \pm 11 \text{ \AA} \end{array}$$

The crystals are built up of MeO_6 octahedra and PO_4 tetrahedra which are linked by corners to form a three-dimensional network. The sodium atoms are octahedrally surrounded by oxygen atoms. A discussion of the structure is given.

Studies on metal phosphates and in particular on transition metal phosphates have been conducted at this Institute for several years¹. In connection with an investigation now in progress of the detailed superstructure of ZrP_2O_7 ² it was found of interest to analyze the atomic arrangement of zirconium phosphates less complex in structure. The mixed phosphate $\text{NaZr}_2(\text{PO}_4)_3$ was selected for such an investigation.

Within the present study the compounds $\text{NaZr}_2(\text{PO}_4)_3$, $\text{NaTi}_2(\text{PO}_4)_3$ and $\text{NaGe}_2(\text{PO}_4)_3$ have been synthesized and found to be isomorphous. Sljukić *et al.* have prepared mixed zirconium and hafnium phosphates of all the alkali metals $\text{AMe}_2^{\text{IV}}(\text{PO}_4)_3$ ³. The X-ray data reported by these authors suggest that all these compounds are isostructural.

EXPERIMENTAL

Preparations of the crystals. A mixture of sodium metaphosphate (12.5 g, British Drug Houses, p.a.) and metal dioxide (1.2 g ZrO_2 , Schering-Kahlbaum, p.a., 1.0 g GeO_2 , Fairmont, p.a. or 0.75 g TiO_2 , Merck, p.a.) was heated in a platinum crucible for 24 hours at $1200^\circ C$.⁴ The products thus obtained were crystalline and gave good X-ray powder patterns but did not contain single crystals well suited for collecting extensive X-ray data. Good crystals could, however, be obtained after tempering in platinum crucible for several weeks at $1100^\circ C$, or according to a method given by Matković *et al.*⁵ by crystallization from a melt of boric acid. The crystals thus obtained were found to consist of colourless, rectangular prisms.

Chemical analysis. A sample of the zirconium compound was fused with sodium potassium carbonate in a platinum crucible. After leaching with boiling water the amount of phosphorus in the solution was determined gravimetrically as $Mg_2P_2O_7$ ⁶. The residue, insoluble in water, was in turn fused with sodium hydrogen sulphate in a platinum crucible. After dissolving in hot water the amount of zirconium was determined gravimetrically as ZrO_2 ⁶. The following data were obtained:

	Calc. for $NaZr_2(PO_4)_3$	Obs.
ZrO_2	50.26	48.5 weight %
P_2O_5	43.43	45.1
Na_2O	6.31	6.4 (residue)

X-ray data collecting and treatment. The powder patterns of the three mixed sodium-transition metal phosphates prepared within this study could all be interpreted assuming a hexagonal (rhombohedral) unit cell. Accurate values of the cell dimensions were calculated from Guinier-Hägg powder photographs taken with strictly monochromatic $CuK\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) with potassium chloride ($a = 6.29228 \text{ \AA}$)⁷ added to the specimens as an internal standard. The hexagonal unit cell dimensions refined by the method of least-squares are ($25^\circ C$):

$\text{NaZr}_2(\text{PO}_4)_2$	$a_H = 8.8043 \pm 2 \text{ \AA}$
	$c_H = 22.7585 \pm 9 \text{ \AA}$
$\text{NaTi}_2(\text{PO}_4)_2$	$a_H = 8.4924 \pm 5 \text{ \AA}$
	$c_H = 21.7788 \pm 15 \text{ \AA}$
$\text{NaGe}_2(\text{PO}_4)_3$	$a_H = 8.1123 \pm 4 \text{ \AA}$
	$c_H = 21.5133 \pm 11 \text{ \AA}$

The value of 3.20 g/cm^3 for the density of $\text{NaZr}_2(\text{PO}_4)_3$, found from the apparent loss of weight in benzene, corresponds to six formula units in the unit cell ($\rho_{\text{calc}} = 3.18 \text{ g/cm}^3$).

Crystals of all the three compounds were studied by taking rotation and Weissenberg photographs which confirmed the presence of strict isomorphism. Complete three-dimensional data were collected for $\text{NaZr}_2(\text{PO}_4)_3$ using $\text{CuK}\alpha$ radiation. The crystal used was a rectangular prism measuring $1.07 \times 10^{-4} \text{ mm}^3$. Multiple film technique was used for the Weissenberg photographs. The relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times. A correction for absorption was included in the computation of the F^2 values. (The linear absorption coefficient $\mu = 234.1 \text{ cm}^{-1}$.)⁸

In the first stages of this structural study the computational work was performed using the computers Facit EDB and TRASK. The limited capacity of these machines made it necessary to conduct the structural refinement with the unit cell described as monoclinic ($C2/c$). All the final calculations, however, made use of the computer CD 3600. This allowed the final structural refinement to be performed with the hexagonal description of the structure.

STRUCTURE DETERMINATION

The Weissenberg data, which confirmed the hexagonal (rhombohedral) symmetry of the crystal, showed the Laue symmetry to be $\bar{3}m$. The reflections systematically absent are $hkil$ with $-h+k+l \neq 3n$ and $h\bar{h}0l$ with $l \neq 2n$. This is characteristic of the space groups $R\bar{3}c$ (No. 167) and $R3c$ (No. 161). A test for piezoelectricity gave no effect. The structural investigation was thus undertaken assuming the atomic arrangement to be in accordance with the higher symmetry $R\bar{3}c$.

In the space group $R\bar{3}c$ (hexagonal axes) the following point positions exist:

$$(000; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3})_+$$

$$6(\underline{a}) (0, 0, \frac{1}{4}; 0, 0, \frac{3}{4})$$

$$6(\underline{b}) (0, 0, 0; 0, 0, \frac{1}{2})$$

$$12(\underline{c}) \pm(0, 0, z; 0, 0, \frac{1}{2}+z)$$

$$18(\underline{d}) (\frac{1}{2}, 0, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$$

$$18(\underline{e}) \pm(x, 0, \frac{1}{4}; 0, x, \frac{1}{4}; x, x, \frac{1}{4})$$

$$36(\underline{f}) \pm(x, y, z; \bar{y}, x-y, z; y-x, \bar{x}, z; \bar{y}, \bar{x}, \frac{1}{2}+z; x, x-y, \frac{1}{2}+z; y-x, y, \frac{1}{2}+z)$$

From calculations of the Patterson projection $P(\underline{pvw})$ and section $P(\underline{Ovw})$ and subsequent calculations of the electron density distributions in $\rho(\underline{pyz})$ and $\rho(\underline{Oyz})$ the positions of the twelve zirconium, the eighteen phosphorus and the six sodium atoms - found to be situated in 12(c), 18(e) and 6(b) - in the unit cell could easily be determined with moderate accuracy. Starting from these data it was possible to make three-dimensional electron density calculations and find the positions of the 72 oxygen atoms situated in 2x36(f) point positions. At the electron density calculations and subsequent refinement atomic scattering curves for un-ionized atoms were used. The real part of the anomalous dispersion correction⁹ was applied to the scattering curves.

A refinement of the coordinates so obtained was then performed by means of the least-squares method. The starting values of the individual isotropic temperature factors used in the program, were zero for all of the atoms. Initially all 296 of the independent reflections measured were included in the calculations, but after a few cycles, eight strong, low-angle reflections were omitted as suffering from extinction. The refinement was considered as complete when the parameter shifts were less than 5% of the standard deviations, at which stage the discrepancy index R was 0.089. Hughes' weighting function $w = 1/h^2 |F_{\text{obs}, \text{min}}|^2$ for $|F_{\text{obs}}| \leq h |F_{\text{obs}, \text{min}}|$ and $w = 1/|F_{\text{obs}}|^2$ for $|F_{\text{obs}}| > |F_{\text{obs}, \text{min}}|$ with $h = 4.0$ was used in the refinement. A weight analysis obtained in the final cycle is given in Table 4.

A list of the observed and calculated structure factors is given in Table 5. A three-dimensional difference synthesis calculated over the unique part of the unit cell at points 0.2 Å apart showed very small maxima and minima. The largest maximum in this synthesis has a magnitude of about 20 % of the heights of the oxygen peaks in the electron density functions. Thus, from this calculation as well as from a computation of the interatomic distances (cf. Table 6), which were found to be within the normal range, further evidence was obtained that the atomic parameters arrived at in the final cycle of refinement and listed in Table 7 should present an adequate description of the structure. Also an attempt to improve the structure by lowering the symmetry to $R\bar{3}c$ was unsuccessful.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The crystal structure of $\text{NaZr}_2(\text{PO}_4)_3$ thus derived may be described in terms of PO_4 tetrahedra and ZrO_6 octahedra which are linked by corners to a three-dimensional network (cf. Fig. 1). Every oxygen atom thus belongs simultaneously within a PO_4 group and a ZrO_6 group. The sites of the sodium atoms are in the strongly distorted octahedra formed by the triangular faces of two ZrO_6 octahedra stacked on top of each other as illustrated in Fig. 2. The groups $\text{O}_3\text{ZrO}_3\text{NaO}_3\text{ZrO}_3$ thus formed may be considered as major structural units of the atomic arrangement. Such groups are mutually linked in the c direction by PO_4 tetrahedra in such a way that empty trigonal prisms of oxygen atoms are formed. The endless columns resulting from this linking are also connected normal to the c direction by the PO_4 tetrahedra (cf. Fig. 1).

All the interatomic distances are of normal lengths (cf. Table 6). The PO_4 tetrahedra are nearly regular. The P-O distances are comparable to those found by Furberg¹⁰ in H_3PO_4 and also by Cruickshank¹¹ and Kierkegaard¹² in several phosphate structures.

Rather few zirconium oxygen compounds have been found to contain ZrO_6 octahedra, more frequent coordination numbers of oxygen around this metal being seven (e.g. in ZrO_2 , monoclinic¹², and $Zr_4(OH)_6(CrO_4)_5 \cdot 2H_2O$ ¹⁴) or eight (e.g. in ZrO_2 , cubic¹⁵, $Zr(SO_4)_2 \cdot 4H_2O$ ¹⁶, $Zr(IO_3)_4$ ¹⁷ and $ZrOCl_2 \cdot 8H_2O$ ¹⁸). The Zr-O distances of the somewhat distorted octahedra (Fig. 3b) of $NaZr_2(PO_4)_3$ (2.048 and 2.084 Å) are somewhat shorter than the value 2.097 Å reported for $BaZrO_3$ ¹⁸ of perovskite type structure.

The six-fold coordination of oxygen around sodium (Fig. 3c) represents a heavily distorted octahedron with O-Na-O angles of 66.0° and 114.0° .

Acknowledgements. This investigation has been sponsored in part by the Swedish Natural Science Research Council and in part by the European Research Office, United States Army, Frankfurt am Main, Germany. Permission for the use of the computers Facit EDB, TRASK and CD 3600 was granted by the Computer Division of the National Swedish Rationalization Agency.

The authors sincerely thank Professor Arne Magnéli for his encouraging and stimulating interest and for all facilities placed at their disposal. They are also indebted to Mr. Lars Tallbacka for his willing help in the measurement of the piezoelectric effect.

REFERENCES

1. Kierkegaard, P. Arkiv Kemi 19 (1962) 51.
2. Levi, G.R. and Peyronell, G. Z. Krist. 92 (1935) 190.
3. Sljukić, M. Matković, B. and Prodić, B. Croat. Chem. Acta 39 (1967) 145.
4. Gmelin's Handbuch, 8 ed. System No. 42, 410
Verlag Chemie, Weinheim/Bergstrasse 1958.
5. Matković, B., Sljukić, M. and Prodić, B. Croat. Chem. Acta 38 (1967) 69.
6. De Hevesy, G. and Kimura, Angew. Chem. 38 (1925) 775.
7. Hambling, P.G. Acta Cryst. 6 (1953) 98.
8. International Tables for X-Ray Crystallography, Vol. III,
Birmingham 1962.
9. Dauben, C.H. and Tempelton, D.H. Acta Cryst. 8 (1955) 841.
10. Furberg, S. Acta Chem. Scand. 9 (1955) 1557.
11. Cruickshank, D.W.J. Acta Cryst. 17 (1964) 671.
12. Nord, A.G. and Kierkegaard, P. Acta Chem. Scand. 22 (1968)
13. McCullough, J.D. and Trueblood, K.N. Acta Cryst. 12 (1959) 507.
14. Lundgren, G. Arkiv Kemi 13 (1958) 59.
15. Passerini, L. Gazz. Chim. Ital. 60 (1930) 672.
16. Singer, J. and Cromer, D.T. Acta Cryst. 12 (1959) 719.
17. Larson, A.C. and Cromer, D.T. Acta Cryst. 14 (1961) 128.
18. Clearfield, A. and Vaughan, P.A. Acta Cryst. 9 (1956) 555.
19. Megav, H.D. Proc. Phys. Soc. 58 (1946) 133.

Table 1. X-Ray Powder Data of $\text{NaGe}_2(\text{PO}_4)_3$. $\text{CuK}\alpha$ radiation.
 ($\lambda_{\text{CuK}\alpha} = 1.54056$)

<u>h</u>	<u>k</u>	<u>l</u>	Obs.	Calc.	Delta	D _{obs}	I ₀
0	1	2	1697	1715	-18	5.91	s
1	0	4	3237	3253	-16	4.28	vs
1	1	0	3601	3606	-5	4.06	vs
1	1	3	4752	4760	-8	3.53	vs
0	2	4	6835	6860	-25	2.95	vs
1	1	6	8201	8221	-20	2.69	vs
2	1	1	8537	8543	-6	2.64	s
0	1	8	9391	9407	-16	2.51	m
2	1	4	10450	10466	-16	2.38	s
3	0	0	10801	10819	-18	2.34	vs
2	0	8	13009	13013	-4	2.14	m
1	1	9	13971	13990	-19	2.06	m
2	2	0	14434	14425	9	2.03	m
2	1	7	14694	14696	-2	2.01	w
3	0	6	15429	15434	-5	1.96	m
2	2	3	15569	15579	-10	1.95	w
3	1	2	16145	16140	5	1.92	m
1	2	8	16613	16619	-6	1.89	s
0	2	10	17617	17628	-11	1.84	s
0	0	12	18469	18461	8	1.79	m
2	2	6	19041	19040	1	1.77	s
0	4	2	19744	19747	-3	1.73	s
2	1	10	21229	21235	-6	1.67	vs
1	3	7	21883	21909	-26	1.65	m
3	2	1	22969	22968	1	1.61	w
3	1	8	23828	23832	-4	1.58	s
3	2	4	24892	24891	1	1.54	s
4	1	0	25250	25244	6	1.53	s
2	3	5	26059	26045	14	1.51	vw
0	1	14	26323	26329	-6	1.50	m
0	4	8	27416	27438	-22	1.47	m
1	3	10	28450	28447	3	1.44	s
3	0	12	29272	29280	-8	1.42	w
2	3	8	30989	31040	-51	1.38	w
3	1	11	31134	31139	-5	1.38	vw
4	0	10	32065	32054	11	1.36	s
0	5	4					
1	1	15					
3	3	0					
1	2	14	32446	32451	-5	1.35	s
3	2	10	33558	33542	16	1.33	m
2	4	4	35684	35660	24	1.29	m
5	1	4	39350	39317	33	1.23	m
3	1	14	40767	40754	13	1.21	w
2	1	16	41235	41234	1	1.20	vw
0	0	18	41550	41536	14	1.19	w
6	0	0	43270	43270	0	1.17	m

Table 2. X-Ray Powder Data of $\text{NaTi}_2(\text{PO}_4)_3$. $\text{CuK}\alpha_1$ radiation.
 $(\lambda_{\text{CuK}\alpha_1} = 1.54056)$

<u>h</u>	<u>k</u>	<u>l</u>	Obs.	Calc.	Delta	D_{obs}	$\frac{I}{I_0}$
0	1	2	1606	1597	9	6.08	s
1	0	4	3099	3098	1	4.38	vs
1	1	0	3295	3291	4	4.24	vs
1	1	3	4420	4417	3	3.66	vs
2	0	2	4895	4888	7	3.48	vw
0	2	4	6388	6389	-1	3.05	vs
1	1	6	7803	7804	-1	2.76	vs
2	1	1					
2	1	4	9700	9680	20	2.47	s
3	0	0	9883	9872	11	2.45	m
2	0	8	12383	12394	-11	2.19	m
1	1	9	13403	13423	-20	2.10	w
2	1	7	13810	13808	2	2.07	vw
2	2	3	14276	14289	-13	2.04	w
3	0	6	14364	14376	-12	2.03	m
1	3	1					
1	2	8	15665	15684	-19	1.95	s
1	3	4	16256	16262	-6	1.91	s
0	2	10	16908	16897	11	1.87	s
2	2	6	17684	17666	18	1.83	m
2	1	10	20184	20188	-4	1.71	s
1	3	7	20401	20390	11	1.71	m
3	1	8	22278	22266	12	1.63	s
3	2	4	22838	22843	-5	1.61	s
4	1	0	23027	23035	-8	1.61	m
4	1	3	24175	24161	14	1.57	m
0	4	8	25582	25557	25	1.52	s
0	1	14					
1	3	10	26793	26769	24	1.49	s
4	1	6	27587	27539	48	1.47	m
3	0	12	27898	27886	12	1.46	w
5	0	12	28914	28906	8	1.43	s
2	0	14					
3	1	11	29443	29425	16	1.42	m
0	5	4					
1	2	14	32188	32196	-8	1.36	m
3	3	6	34163	34130	33	1.32	w
5	1	1					
1	5	5	37106	37132	-26	1.26	w
4	2	8	38764	38778	-14	1.24	w
3	1	14					
6	0	0	39497	39489	8	1.23	m

Table 3. X-Ray Powder Data of $\text{NaZr}_2(\text{PO}_4)_3$. $\text{CuK}\alpha$ radiation.
 ($\lambda_{\text{CuK}\alpha} = 1.54056$)

<u>h</u>	<u>k</u>	<u>l</u>	Obs.	Calc.	Delta	D _{obs}	I _o
0	1	2	1488	1479	9	6.31	s
1	0	4	2862	2853	9	4.55	vs
1	1	0	3073	3062	11	4.39	vs
1	1	3	4104	4093	11	3.80	vs
0	2	4	5921	5915	6	3.17	vs
1	1	6	7194	7186	8	2.87	vs
2	1	1	7262	7259	3	2.86	s
0	1	8	8353	8352	1	2.67	m
2	1	4	8983	8977	6	2.57	s
3	0	0	9188	9185	3	2.54	vs
2	0	8	11411	11414	-3	2.26	m
2	2	0	12260	12247	13	2.20	m
1	1	9	12338	12341	-3	2.19	m
1	0	10	12478	12476	2	2.18	m
2	1	7	12753	12757	-4	2.16	w
3	0	6	13305	13309	-4	2.11	s
3	1	2	13711	13726	-15	2.08	w
1	2	8	14487	14476	11	2.02	s
1	3	4	15118	15100	18	1.98	s
0	2	10	15528	15538	-10	1.95	s
3	1	5	16122	16131	-9	1.92	w
2	2	6	16372	16371	1	1.90	vs
0	0	12	16497	16496	1	1.90	w
0	4	2	16772	16787	-15	1.88	m
4	0	4	18160	18162	-2	1.81	w
2	1	10	18615	18599	16	1.79	vs
1	3	7	18889	18881	8	1.77	m
3	2	1	19491	19506	-15	1.74	vw
3	1	8	20603	20599	4	1.70	s
3	2	4	21229	21224	5	1.67	s
4	1	0	21470	21432	38	1.66	vs
2	2	9	21522	21526	-4	1.66	vw
2	3	5	22287	22255	32	1.63	m
4	1	3	22425	22463	-38	1.63	m
0	1	14	23492	23473	19	1.59	m
0	4	8	23657	23661	-4	1.58	m
1	3	10	24724	24723	1	1.55	s
3	2	7	25000	25004	-4	1.54	vw
4	1	6	25560	25556	4	1.52	s
3	0	12	25686	25681	5	1.52	w
2	0	14	26538	26535	3	1.50	s
2	3	8	26726	26722	4	1.49	w

<u>h</u>	<u>k</u>	<u>l</u>	Obs.	Calc.	Delta	D _{obs}	I _o
3	1	11	27132	27129	3	1.48	VW
0	5	4	27344	27347	-3	1.47	m
3	3	0	27550	27556	-6	1.47	m
4	0	10	27791	27785	6	1.46	m
3	3	3	28580	28587	-7	1.44	VW
1	1	15	28846	28836	10	1.43	m
1	2	14	29603	29597	6	1.42	s
1	0	16	30300	30346	-46	1.40	m
4	1	9	30706	30711	-5	1.39	VW
3	2	10	30851	30846	5	1.39	m
3	3	6	31675	31680	-5	1.37	m
5	1	1	31744	31752	-8	1.37	w
1	3	13	32603	32627	-24	1.35	VW
5	1	4	33481	33471	10	1.33	s
2	4	7	34186	34189	-3	1.32	VVW
1	5	5	34506	34502	4	1.31	VW
3	1	14	35726	35720	6	1.29	m
2	1	16	36463	36470	-7	1.28	w
6	0	0	36731	36741	-10	1.27	m
0	0	18	37104	37116	-12	1.26	w
5	1	7	37245	37251	-6	1.26	w
2	5	2	38216	38220	-4	1.25	w
4	3	4	39613	39594	19	1.22	w
5	2	0	39797	39803	-6	1.22	m
2	4	10	40042	40032	10	1.22	m
6	0	6	40872	40865	7	1.20	w
2	3	14	41858	41844	14	1.19	m
5	1	10	43102	43093	9	1.17	VW
5	2	6	43925	43927	-2	1.16	m
2	5	8	45103	45093	10	1.15	m
1	5	11	45502	45499	3	1.14	w
1	6	4	45710	45718	-8	1.14	w
3	0	18	46319	46301	18	1.13	w
4	1	15	47213	47207	6	1.12	w
3	2	16	48707	48717	-10	1.10	w
4	4	0	48970	48988	-18	1.10	w

Table 4. Weight analyses obtained in the final cycle of the least-squares refinement of $\text{NaZr}_2(\text{PO}_4)_3$

Interval $\sin \theta$	Number of independent reflections	$\overline{w \Delta^2}$	Interval F_{obs}	Number of independent reflections	$\overline{w \Delta^2}$
0.0000-0.4642	30	1.36	0.0- 23.1	28	0.14
0.4642-0.5848	36	0.98	23.1- 31.3	29	0.47
0.5848-0.6694	30	0.58	31.3- 52.2	29	1.22
0.6694-0.7368	35	0.80	52.2- 63.4	29	1.06
0.7368-0.7937	27	1.02	63.4- 82.5	29	1.61
0.7937-0.8434	22	0.47	82.5- 99.6	29	1.28
0.8434-0.8879	36	0.85	99.6-115.5	28	1.14
0.8879-0.9283	23	1.13	115.5-143.3	30	1.18
0.9283-0.9655	30	0.97	143.3-192.1	28	0.61
0.9655-1.0000	19	1.84	192.1-345.3	29	1.29

IV:13

Table 5. Observed and calculated structure factors. The 5 columns within each group contain the values h , k , l , F_o and $k|F_o|$. The reflections deleted from the final cycles in the least-squares refinement are marked with an *.

0	0	0	0	-	1	0	10	-137	100	3	2	7	-70	80	5	1	10	-71	60
0	0	12	235	190	1	0	13	11	-	3	2	10	-192	100	5	1	13	-60	90
0	0	18	-370	200	1	0	16	-90	60	3	2	13	60	75	5	1	16	-90	90
0	0	24	-54	54	1	0	19	-3	-	3	2	16	-105	102	5	1	19	90	60
0	1	2	-137	150	1	7	0	191	137	3	2	19	-37	20	5	1	22	71	80
0	1	8	119	119	1	7	3	30	-	3	2	22	62	31	5	2	0	192	201
0	1	14	269	251	1	7	6	123	123	3	2	25	25	31	5	2	3	-20	20
0	1	20	212	204	1	7	9	0	-	3	3	0	270	207	5	2	6	106	102
0	1	26	46	39	1	7	12	13	-	3	3	3	-72	87	5	2	9	16	-
0	2	4	-377	329	1	7	15	20	21	3	3	6	160	132	5	2	12	-2	-
0	2	10	-293	256	1	7	18	-90	30	3	3	9	-6	-	5	2	15	-25	37
0	2	16	-122	113	1	7	21	-9	-	3	3	12	42	34	5	2	18	-66	67
0	2	22	79	87	1	7	24	-36	32	3	3	15	-30	52	5	2	21	-80	29
0	2	28	92	144	1	7	27	62	65	3	3	18	-100	104	5	2	24	-35	20
0	3	0	426	363	1	7	30	33	32	3	3	21	26	35	5	2	27	35	89
0	3	6	204	204	1	7	33	-2	-	3	3	24	-84	91	5	2	30	105	89
0	3	12	107	125	1	7	36	-92	90	3	4	2	-90	107	5	2	33	-25	20
0	3	18	-153	157	2	0	0	39	47	3	4	5	-20	30	5	2	36	130	121
0	3	24	-95	123	2	0	3	187	193	3	4	8	190	205	5	2	39	75	20
0	4	2	-193	270	2	0	6	325	330	3	4	11	47	65	5	2	42	85	63
0	4	8	218	244	2	0	9	134	129	3	4	14	124	103	5	4	1	-36	27
0	4	14	132	124	2	0	12	46	65	3	4	17	12	-	5	4	4	-150	167
0	4	20	200	191	2	1	1	-146	209	3	4	20	134	153	5	4	7	32	24
0	4	26	2	-	2	1	4	-224	242	3	4	23	35	31	5	4	10	-80	87
0	5	4	-295	265	2	1	7	-13	60	3	4	26	121	121	5	4	13	-35	-
0	5	10	-93	64	2	1	10	-327	344	3	5	1	-22	30	5	4	16	-61	61
0	5	16	-92	109	2	1	13	13	-	3	5	4	-152	156	5	4	19	132	147
0	5	22	69	95	2	1	16	-90	87	3	5	7	23	-	5	4	22	29	25
0	6	0	360	367	2	1	19	43	-	3	5	10	-64	78	5	4	25	112	117
0	6	6	104	120	2	1	22	47	35	3	5	13	-17	17	5	4	28	-21	23
0	6	12	57	54	2	1	25	7	-	3	5	16	144	134	5	4	31	-19	30
0	6	18	-152	145	2	2	0	163	132	3	6	0	7	-	5	4	34	-15	13
0	7	2	-109	121	2	2	3	90	95	3	6	3	105	97	5	4	37	27	20
0	7	8	177	179	2	2	6	345	270	3	6	6	23	21	4	6	4	94	100
0	7	14	62	71	2	2	9	74	79	3	6	9	-5	-	4	6	7	51	50
0	7	20	136	100	2	2	12	-65	37	3	6	12	-4	-	4	6	10	-151	169
0	8	4	-147	153	2	2	15	10	-	3	7	15	-9	-	6	1	2	-33	57
0	8	10	-126	115	2	2	18	-37	35	3	7	18	9	-	6	1	5	77	-
0	8	16	-60	54	2	2	21	-5	-	3	7	21	40	95	6	1	8	115	102
0	8	22	115	115	2	2	24	-151	102	3	7	24	-20	20	6	1	11	-32	-
0	9	0	112	115	2	2	27	-27	12	4	0	4	-94	109	6	1	14	139	143
0	9	6	-322	224	2	3	2	12	74	4	0	7	-250	261	6	1	17	8	-
0	9	12	-155	147	2	3	5	78	74	4	0	10	-4	-	6	1	20	113	101
0	9	18	-80	74	2	3	8	154	130	4	0	13	-2	-	6	2	1	35	29
0	9	24	61	65	2	3	11	-90	35	4	1	16	105	105	6	2	4	-100	101
0	10	0	28	83	2	3	14	244	245	4	1	19	225	252	6	2	7	-75	57
0	10	6	104	101	2	3	17	26	-	4	1	22	-71	84	6	2	10	-117	110
0	10	12	290	234	2	3	20	107	103	4	1	25	-2	-	6	2	13	51	44
0	10	18	-110	123	2	3	23	-26	-	4	1	28	47	52	6	2	16	-62	84
0	11	0	12	30	2	4	1	9	-	4	1	31	-124	121	6	2	19	-24	21
0	11	6	150	165	2	4	4	-178	188	4	1	34	-65	60	6	2	22	-13	-
0	11	12	-90	85	2	4	7	66	51	4	1	37	-110	143	6	2	25	174	126
0	11	18	-90	99	2	4	10	-170	186	4	1	40	-24	27	6	2	28	27	22
0	11	24	-90	99	2	4	13	-51	56	4	2	5	-54	57	6	2	31	1	-
0	11	30	-161	176	2	4	16	81	79	4	2	8	122	130	6	2	34	0	-
0	12	0	27	31	2	4	19	12	-	4	2	11	34	44	6	2	37	-64	66
0	12	6	-3	-	2	4	22	41	64	4	2	14	101	105	6	2	40	-5	-
0	12	12	-3	-	2	4	25	-51	52	4	2	17	11	-	6	2	43	81	89
0	12	18	300	-	2	5	0	194	161	4	2	20	115	120	6	2	46	11	20
0	12	24	21	-	2	5	3	27	42	4	2	23	18	20	6	2	49	36	28
0	13	0	206	206	2	5	6	-12	-	4	3	1	12	-	6	3	4	-101	96
0	13	6	-74	70	2	5	9	-23	20	4	3	4	-107	116	7	0	4	-37	-
0	13	12	130	147	2	5	12	-72	87	4	3	7	67	81	7	0	7	-215	102
0	13	18	23	-	2	5	15	23	27	4	3	10	-249	221	7	0	10	-8	-
0	13	24	27	37	2	5	18	20	-	4	3	13	-29	33	7	1	13	36	-
0	14	0	27	37	2	6	2	20	-	4	3	16	-10	-	7	1	16	34	95
0	14	6	45	45	2	6	5	59	60	4	3	19	-2	-	7	1	19	2	-
0	14	12	231	231	2	6	8	65	65	4	3	22	4	-	7	1	22	5	-
0	14	18	-130	130	2	6	11	-63	61	4	4	0	177	204	7	1	25	19	15
0	14	24	-200	201	2	6	14	174	105	4	4	3	-20	22	7	1	28	-64	42
0	15	0	61	61	2	6	17	24	17	4	4	6	133	116	7	1	31	-12	-
0	15	6	99	42	2	7	1	-25	23	4	4	9	-16	-	7	2	34	2	-
0	15	12	-99	42	2	7	4	-110	117	4	4	12	9	-	7	2	37	78	74
0	15	18	29	30	2	7	7	-17	16	4	4	15	-7	-	7	2	40	-10	-
0	15	24	34	-	2	7	10	-122	114	4	4	18	-73	66	7	2	43	117	90
0	16	0	360	362	2	8	0	0	-	4	5	2	-9	-	7	3	1	14	-
0	16	6	62	61	2	8	3	106	106	4	5	5	-43	26	7	3	4	-60	55
0	16	12	224	205	2	8	6	26	26	4	5	8	60	37	7	3	7	-25	25
0	16	18	-30	97	2	8	9	91	83	4	5	11	27	23	7	3	10	-136	179
0	16	24	-6	-	2	8	12	-19	22	4	5	14	149	153	7	4	13	-4	-
0	17	0	50	50	3	0	0	149	143	4	5	17	-22	19	8	0	2	-16	-
0	17	6	-122	131	3	0	3	-164	130	4	6	0	-23	23	8	0	5	77	80
0	17	12	-26	76	3	0	6	-77	80	4	6	3	-70	62	8	0	8	140	113
0	17	18	-119	132	3	0	9	-77	80	4	6	6	-70	62	8	1	1	-60	51
0	17	24	-2	-	3	1	1	-81	100	4	6	9	10	15	8	1	4	-109	119
0	18	0	92	92	3	1	4	71	86	4	7	0	-115	134	8	1	7	-34	-
0	18	6	25	-	3	1	7	221	275	4	7	3	9	-	8	1	10	-103	106
0	18	12	100	102	3	1	10	-93	101	4	7	6	149	152	8	1	13	34	-
0	18	18	223	240	3	1	13	-217	241	4	8	0	-37	42	8	1	16	-27	-
0	18	24	-64	60															

Table 6. Interatomic distances and estimated standard deviations
($\pm \sigma$) in Å.

Zr - O	Zr - 3 O ₁	=	2.048	\pm	13	
	Zr - 3 O ₂	=	2.084	\pm	12	
P - O	P - 2 O ₁	=	1.516	\pm	13	
	P - 2 O ₂	=	1.546	\pm	13	
Na - O	Na - 6 O ₂	=	2.538	\pm	12	
	Na - 6 O ₁	=	3.689	\pm	13	
O - O	O ₁ - 4 O ₂	=	2.48	\pm	2	; 2.52 \pm 2
	(O ₂ - 4 O ₂)	=	2.94	\pm	2	; 3.01 \pm 2
	O ₁ - 4 O ₁	=	2.50	\pm	2	; 2 x 2.96 \pm 2
			3.21	\pm	2	
	O ₂ - 3 O ₂	=	2.52	\pm	2	; 2 x 2.761 \pm 2

Additional distances

Zr - Na(Na-2Zr)	=	3.315	\pm	2
Zr - 3 P(P-2Zr)	=	3.444	\pm	3
Zr - 3 P(P-2Zr)	=	3.493	\pm	5
P - 2 Na(Na-6P)	=	3.667	\pm	3

Table 7. The structure of $\text{NaZr}_2(\text{PO}_4)_3$.Space group: $\underline{R}\bar{3}/\underline{c}$

Unit cell dimensions: $\underline{a} = 8.8043 \pm 2 \text{ \AA}$
 $\underline{c} = 22.7585 \pm 9 \text{ \AA}$
 $\underline{V} = 1527.7 \text{ \AA}^3$

Cell content: 6 $\text{NaZr}_2(\text{PO}_4)_3$ 6 Na in 6(b): $(0, 0, 0; 0, 0, \frac{1}{2})$ 12 Zr in 12(c): $\pm(0, 0, \underline{z}; 0, 0, \frac{1}{2} + \underline{z})$ 18 P in 18(e): $\pm(\underline{x}, 0, \frac{1}{4}; 0, \underline{x}, \frac{1}{4}; \bar{\underline{x}}, \bar{\underline{x}}, \frac{1}{4})$ 36 O_1 and 36 O_2

in 2x36(f): $\pm(\underline{x}, \underline{y}, \underline{z}; \bar{\underline{y}}, \underline{x} - \underline{y}, \underline{z}; \underline{y} - \underline{x}, \bar{\underline{x}}, \underline{z}; \bar{\underline{y}}, \bar{\underline{x}}, \frac{1}{2} + \underline{z};$
 $\underline{x}, \underline{x} - \underline{y}, \frac{1}{2} + \underline{z}; \underline{y} - \underline{x}, \underline{y}, \frac{1}{2} + \underline{z})$

Atomic parameters and isotropic temperature factors with estimated standard deviations ($\pm \sigma$).

Atom	\underline{x}	\underline{y}	\underline{z}	$\underline{B} \text{ \AA}^2$
Na	0	0	0	4.20 ± 40
Zr	0	0	0.1456 ± 1	1.80 ± 7
P	0.2909 ± 6	0	$\frac{1}{4}$	2.40 ± 10
O_1	0.1860 ± 15	-0.0144 ± 15	0.1949 ± 5	3.20 ± 20
O_2	0.1913 ± 15	0.1683 ± 15	0.0866 ± 5	2.90 ± 20

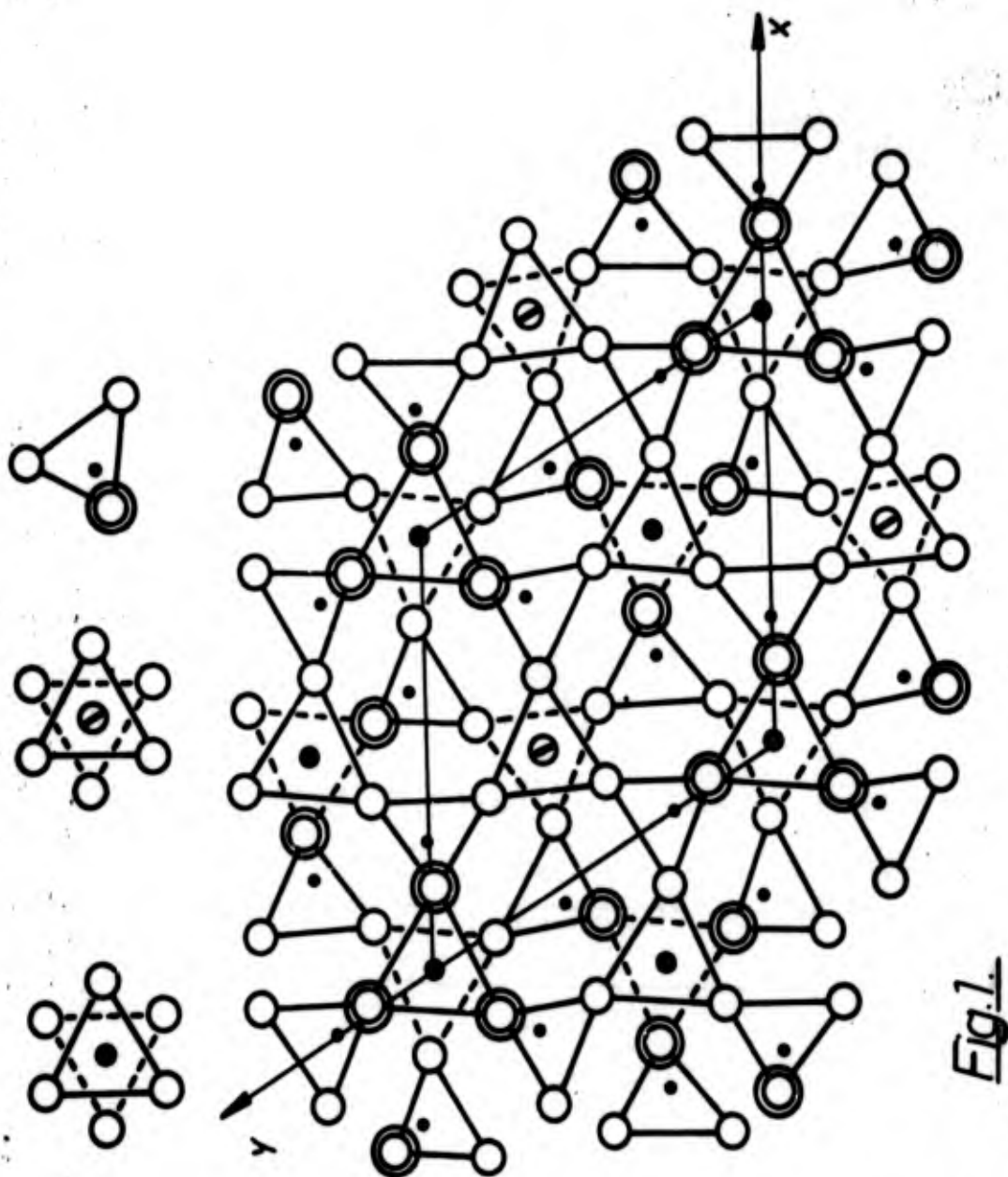


Fig. 1.

Fig. 1. Schematic drawing showing the structure of $\text{NaZr}_2(\text{PO}_4)_5$. The structure viewed along $[001]$ showing the contacts between PO_4 tetrahedra, ZrO_6 octahedra and NaO_6 octahedra. Only one third of the structure has been indicated (i.e. atoms with z parameters within the limits $0.00 \leq z \leq 0.33$).

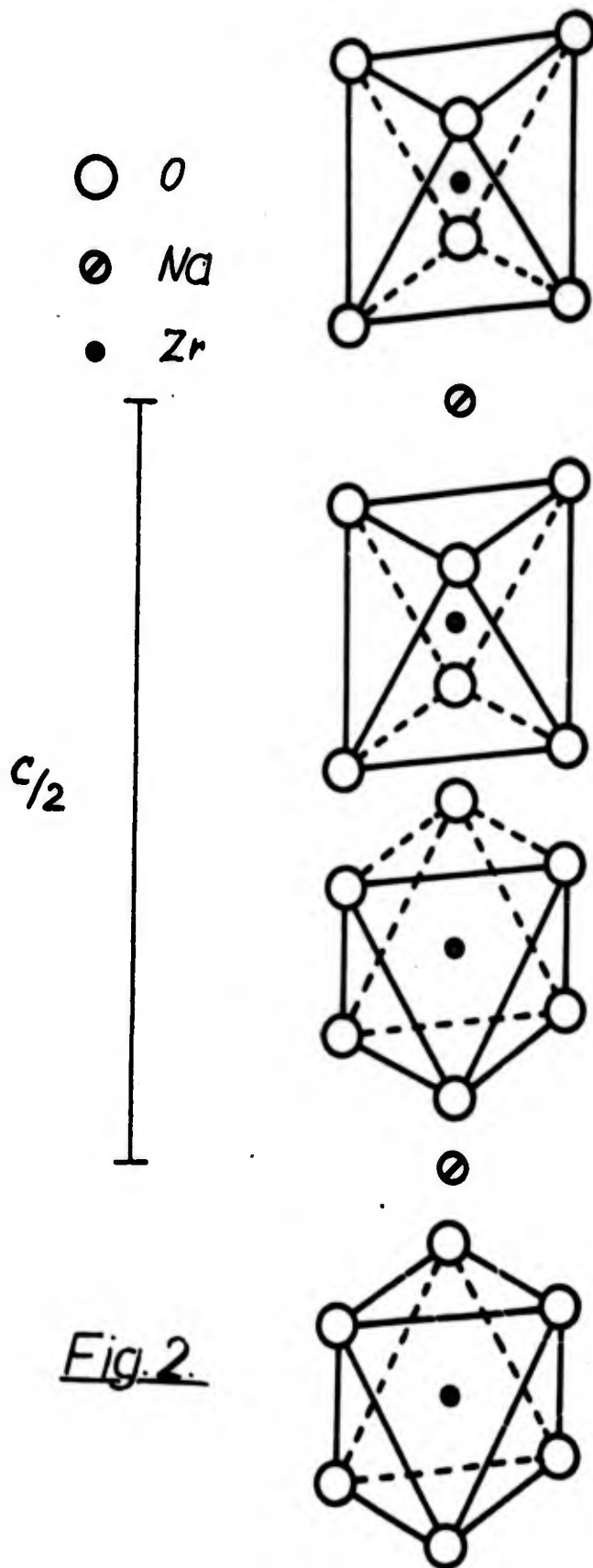


Fig. 2. Schematic drawing showing the sites of the sodium atoms between ZrO_6 octahedra in the structure of $NaZr_2(PO_4)_3$.

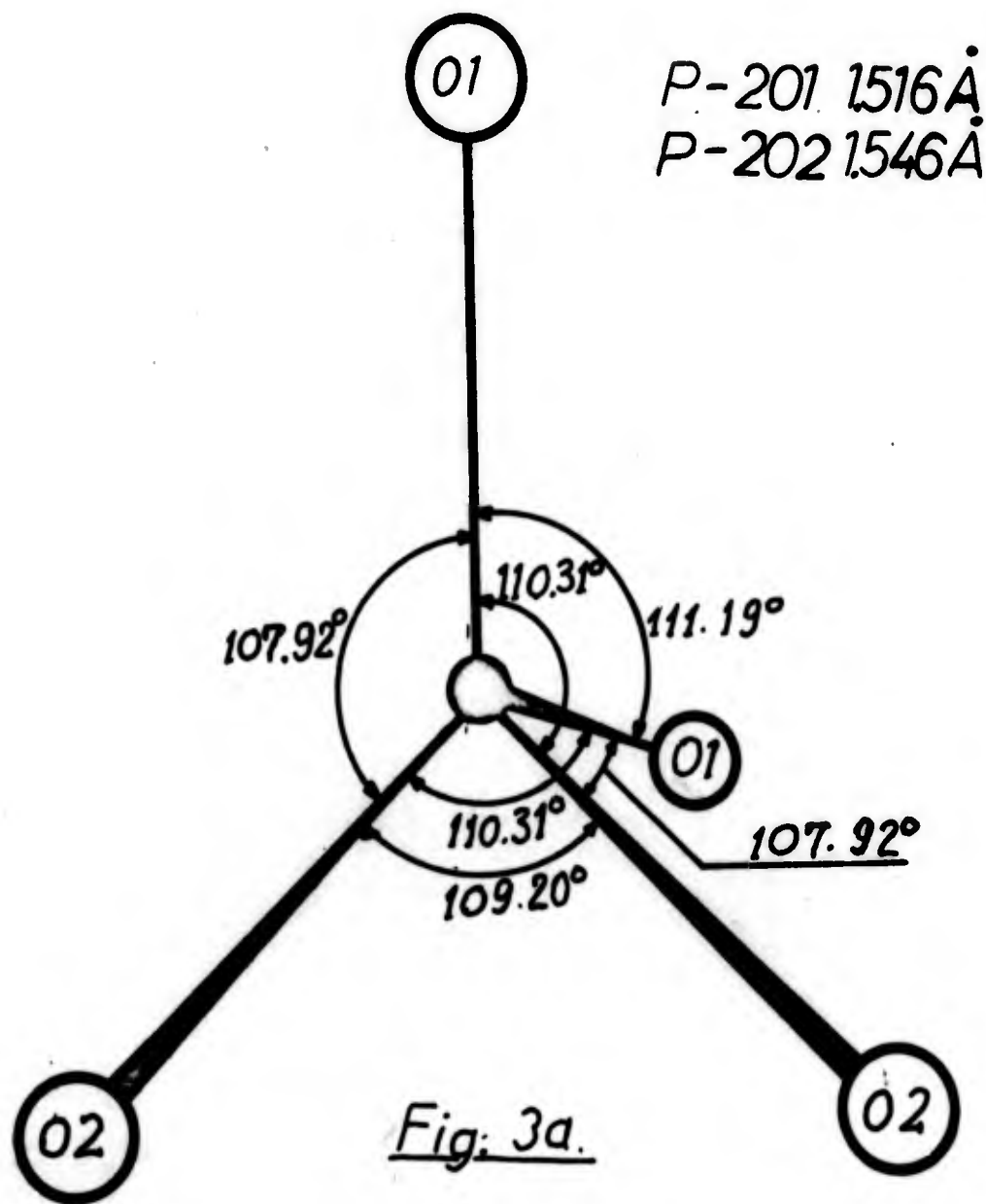


Fig. 3a. The PO_4 tetrahedron in the structure of $NaZr_2(PO_4)_3$.

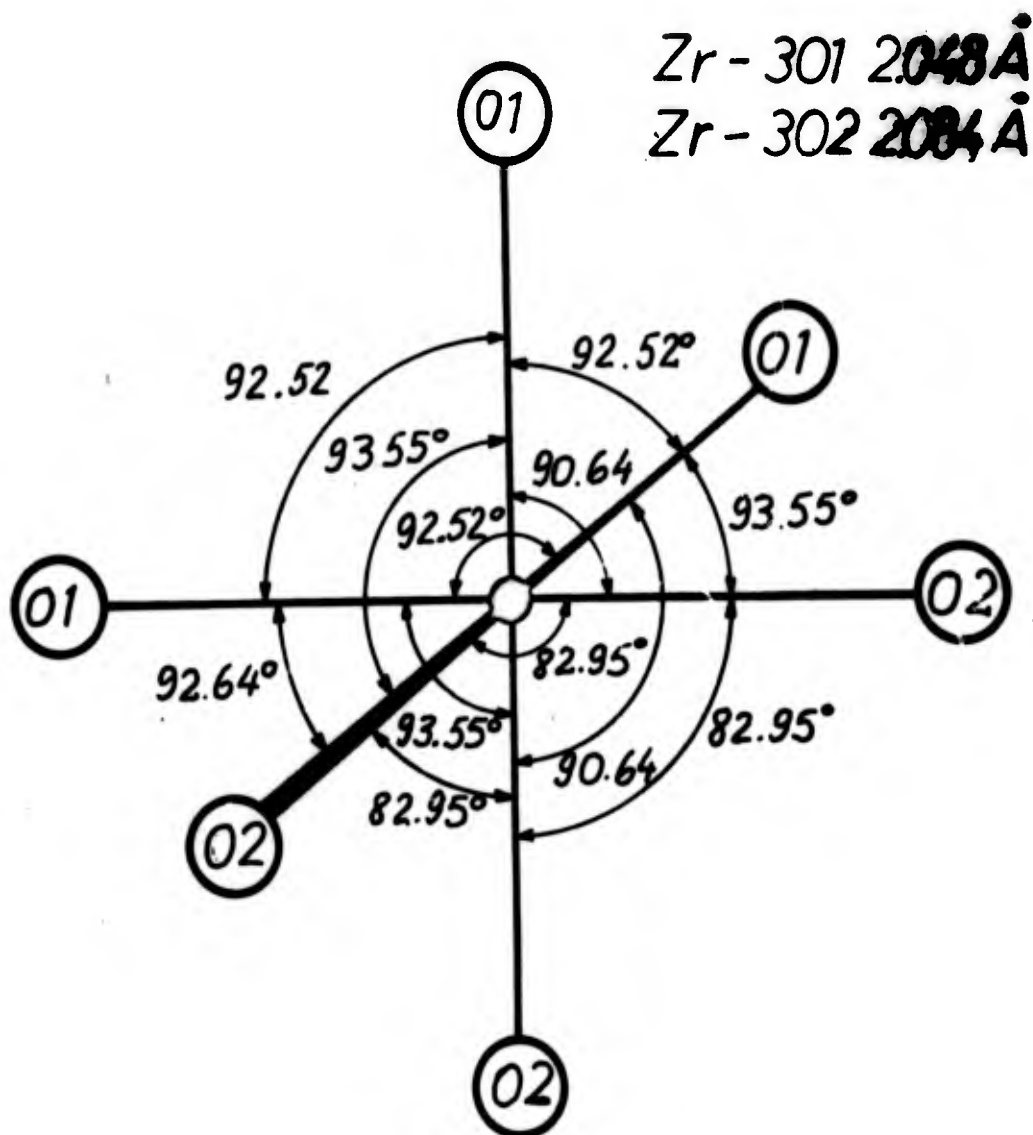


Fig. 3b.

Fig. 3b. The ZrO₆ octahedron in the structure of NaZr₂(PO₄)₃.

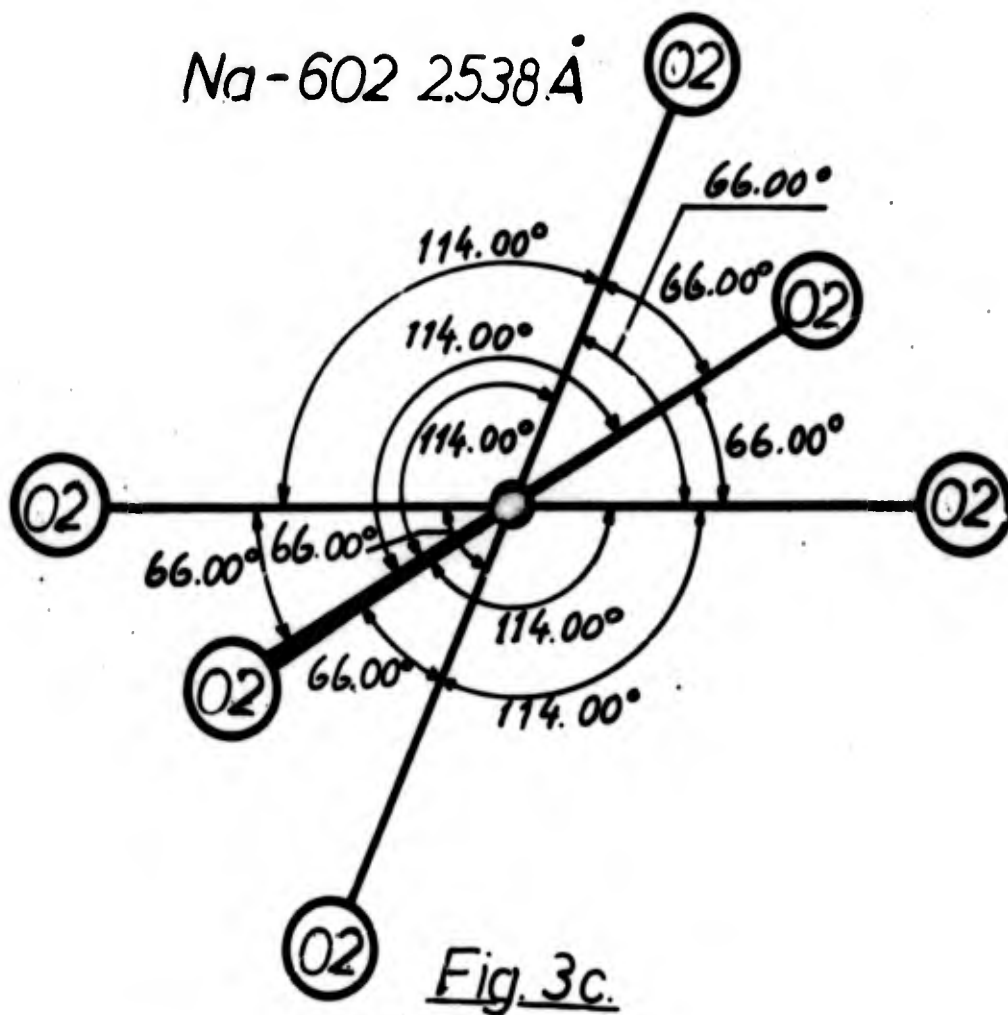


Fig. 3c. The NaO_6 octahedron in the structure of $\text{NaZr}_2(\text{PO}_4)_3$.

The Crystal Structure of a New Copper Wolfram Oxide, Cu_3WO_6

ELIZABETH GEBERT* and LARS KIHNBORG

Institute of Inorganic and Physical Chemistry, University of Stockholm,
Stockholm Va, Sweden

The crystal structure of the previously unknown phase Cu_3WO_6 has been determined and refined from X-ray, single crystal diffractometer data. The symmetry is cubic, space group $\text{Pa}\bar{3} - \frac{T_h^6}{I_h}$ and the unit cell parameter is $a = 9.797 (+3) \text{ \AA}$.

The structure can be described as built up of distorted WO_6 octahedra and CuO_5 triangular bipyramids, which share corners and edges in a rather complicated way. Each octahedron is linked to 6 bipyramids and each bipyramid to 4 octahedra and 6 other CuO_5 bipyramids.

Six CuO_5 bipyramids sharing edges form a staggered ring with $\bar{3}$ symmetry and one WO_6 group on either side of the ring closes the hole in the centre.

Interatomic distances and angles are given.

* *

While many ternary oxide systems involving transition metals have been extensively studied especially in recent years, rather little has been reported about the copper-wolfram-oxygen system. This is somewhat remarkable since the coordination chemistry of both these metals has drawn considerable attention and since there are inherent possibilities for interesting bonding features and physical properties in this system. There are a few papers in recent years reporting on " CuWO_4 "^{1,2}, Cu_xWO_3 ³ and $\text{Cu}_x\text{WO}_{3+6}$ ⁴ but we have not found evidence in the literature for the existence of other intermediate phases in this system.

We have undertaken an investigation of this system by X-ray methods and in the course of this we have observed two phases, both prepared at about 800°C . A preliminary note about one of these, which we prefer to designate by the formula CuWO_{4-x} , but which is probably identical with the phases (phase) mentioned above, has recently been

* On leave from Argonne National Laboratory, Argonne, Ill., USA.

published in this journal.⁵ Our studies on the second phase is reported in this article.

EXPERIMENTAL

Mixtures of CuO and WO_3 of analytical grade were placed in platinum tubes which were evacuated, sealed and heated for 3-5 days at 800°C . Oxygen deficient samples were prepared by substituting Cu_2O or WO_2 for part of the copper(II) or wolfram(VI) oxide, respectively.

The samples were examined microscopically and by taking X-ray powder patterns in a Guinier-type focussing camera using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54051 \text{ \AA}$) and KCl as an internal standard ($a[\text{KCl}, 25^\circ\text{C}] = 6.29228 \text{ \AA}$).⁶ The density was determined pycnometrically on one sample in duplicate runs.

Single crystal photographs were recorded in a Weissenberg camera using CuK radiation. Data for the crystal structure determination were collected with a General Electric manual single crystal orienter equipped with a scintillation counter and using pulse height discrimination. MoK radiation filtered through a niobium foil and the $\theta - 2\theta$ scan technique was used in this case.

Diffractometer settings were made for 976 reflections with $h, k, l \geq 0$ and $\sin^2\theta \leq 0.20$ but after checking of the peak intensity the weakest reflections were rejected and only 653 were actually measured. The scan interval was calculated by the formula $\Delta(2\theta) = 1.65 \pm 1.0 \times \tan\theta$ (degrees), the scan velocity was $0.4^\circ/\text{min}$ in 2θ and the background was counted one minute at the beginning and end of each scan interval. After averaging the measured values for symmetry equivalent reflections there remained a set of 234 non-equivalent intensity data which were used in the subsequent calculations.

IDENTIFICATION AND CHARACTERIZATION OF Cu_3WO_6

The powder patterns of samples with gross compositions around Cu_3WO_6 indicated the presence of a new phase as a major component. The diffraction lines belonging to this phase could be indexed on the basis of a cubic unit cell with $a = 9.79 \text{ \AA}$, approximately. It has not yet been possible to prepare it in a completely pure state but all samples made in this composition region, including those of stoichiometric composition, contained at least traces of CuO and/or CuWO_{4-x} as demonstrated by their powder patterns. The cell constant a calculated from the powder patterns of different samples by least squares refinement falls within the range $9.7936(+2) - 9.8005(+2) \text{ \AA}$ (the errors given within parentheses are single sigma values for each individual pattern). Although no obvious relation between the sample composition and the cell parameter has been found it cannot be excluded that these differences indicate the existence of a narrow homogeneity range for Cu_3WO_6 .

A sample prepared from a mixture of 4 CuO and WO_3 showed faint lines of CuO in addition to those of the new phase. The density of this sample was found to be $\rho_{\text{obs}} = 6.62(+10) \text{ g cm}^{-3}$. The value calculated for Cu_3WO_6 using the observed cell parameter and assuming eight formula units per cell is $\rho_{\text{calc}} = 6.65 \text{ g cm}^{-3}$. Since the density of CuO is approximately 6.4 g cm^{-3} a small amount of this compound as an impurity could not seriously affect the measured density value. It was therefore assumed that the unit cell content is $\text{Cu}_{24}\text{W}_8\text{O}_{48}$ which was proved to be correct by the subsequent structure analysis.

The Cu_3WO_6 phase was formed as black, octahedrally shaped crystals and one of these was selected from a sample of stoichiometric composition for use in the single crystal studies. The powder pattern is listed in Table 1.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The Laue symmetry $m\bar{3}$ was evident in the Weissenberg photographs and from the observation of systematic absences of reflections the space group could be uniquely determined to be $\text{Pa}\bar{3} - T_h^6$ (No. 205). The presence of both 8- and 24-fold positions in this space group was in accordance with the assumed composition and unit cell content.

A three-dimensional Patterson synthesis was calculated from the diffractometer data. Assuming the W atoms to occupy the 8-fold position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ a positional parameter could easily be found which gave rise to W-W vectors that could explain all the strong maxima in this synthesis. The W position thus derived was used in a difference Fourier synthesis from which plausible locations of the copper atoms on one 24-fold position were obtained. After a least squares refinement of the W and Cu positions a second difference synthesis was calculated in which maxima corresponding to oxygen atoms were found. Least squares refinement of these atomic parameters could be successfully performed and the resulting final parameters are given in Table 2.

DETAILS OF THE CALCULATIONS

Computers of the types CD 3200, CD 3600, IBM 360/50 and IBM 1800 were used for the calculations. Among the programs used on these machines the following more important ones may be mentioned; PIRUM for indexing of powder patterns and refinement of cell constants (written by P.-E. Werner, Stockholm), GIP for calculation of diffractometer settings (R. Norrestam, Stockholm), DRP for data reduction and Fourier summations (A. Zalkin, Berkeley, Calif., USA, modified by R. Liminga and J.-O. Lundgren, Uppsala), LALS for full matrix least squares refinement (Gantzel-Sparks-Trueblood, Univ. of Calif., modified by A. Zalkin, J.-O. Lundgren, R. Liminga and C.-I. Brändén), DISTAN for calculation of interatomic distances, angles and standard deviations thereof (A. Zalkin, modified by J.-O. Lundgren and R. Liminga), and ORTEP for making stereo drawings (C.K. Johnson, Oak Ridge, Tenn., USA).

The crystal selected for the data collection was relatively large but its extension varied only between 0.0107 cm and 0.0115 cm in all directions. Its shape ^{could} therefore be approximated by a sphere in the absorption correction of the intensities. A linear absorption coefficient $\mu = 397.5 \text{ cm}^{-1}$ was used in these calculations.

The atomic scattering factors used were those given for un-ionized Cu and W in Ref. 7 and for O in Ref. 8. The complex anomalous dispersion parameters given by Cromer⁹ were applied on the scattering factors of Cu and W.

Weights in the least squares refinement were calculated according to the formula $w = 1/(7000 + |F_{\text{obs}}| - 0.3|F_{\text{obs}}|^2 + 0.45|F_{\text{obs}}|^3)$. The weight analysis obtained in the last cycle is given in Table 3.

It became evident during the refinement that the strongest reflections suffered from extinction since the observed structure amplitudes for these were throughout smaller than the calculated values. The average of the quotient $|F_{\text{obs}}|/|F_{\text{calc}}|$ was 0.80 for the 30 strongest reflections and these were given zero weight in the last few cycles of refinement. The final values of $R = \Sigma ||F_{\text{obs}}| - |F_{\text{calc}}|| / \Sigma |F_{\text{obs}}|$ were 0.065 (the 30 strongest reflections omitted) and 0.120 (including the strong reflections).

The observed and calculated structure amplitudes are listed in Table 4.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of Cu_3WO_6 , illustrated in Fig. 1, is of a type which to our knowledge has not been reported previously. It is quite different from the cubic or pseudocubic alkaline earth wolframates of the same stoichiometry which have been known since long.¹⁰ It can be considered as composed of distorted WO_6 octahedra and CuO_5 "trigonal" bipyramids (the trigonal symmetry is lost by distortion, cf. below). These polyhedra are joined by shared corners or edges in a rather intricate way. Each WO_6 octahedron is coupled to six CuO_5 groups, to three of these by corner-sharing and to the other three by edge-sharing. The WO_6 groups have no oxygen atoms in common although they occur pairwise in the structure with a separation of 3.97 Å between the wolfram atoms along the trigonal axes. Each CuO_5 bipyramid, on the other hand, shares one of the non-equatorial edges (1a-1c, Fig. 2) with a WO_6 octahedron and the three remaining corners with three other octahedra (Fig. 3a). It is also coupled to two other CuO_5 bipyramids by edge-sharing (1b-2a, 1c-2b) and to four additional bipyramids by corner-sharing (Fig. 3b).

Six mutually edge-sharing CuO_5 bipyramids form a ring with the point group symmetry $\bar{3}$ (Fig. 4) and such rings are centered on the equivalent positions $4a$ of this space group $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2})$. The two WO_6 octahedra which form a "pair" (cf. above) both share three

corners with the same bipyramid ring and are situated on opposite sides of the plane (approximate, see below) of the ring on the trigonal axis. The three edges of each octahedron connecting the corners which are not shared with the ring are shared with three other edges in three other bipyramid rings and the WO_6 polyhedra may therefore be considered, formally, to act as a glue for the bipyramid rings.

Interatomic distances and bond angles are listed in Table 5. As was mentioned above, the octahedral coordination around wolfram is not regular but distorted so that only one of the threefold axes remains of the point group symmetry elements. This gives rise to three short and two long W-O bonds and may be looked upon as resulting from a displacement of the metal atom from the centre towards one of the octahedral faces. This 3+3 type coordination seems not to have been reported previously for any wolfram-oxygen compound in which the W-O distances have been determined with sufficient accuracy. Hexavalent wolfram is often tetrahedrally coordinated by oxygen but distorted octahedral coordination is also rather common. It occurs for example in WO_3 and in ternary oxides of the wolframite type (for instance $NiWO_4$ ¹¹, $CdWO_4$ ¹² and $CuWO_4$ ⁵). In these latter cases the distortion gives rise to a group of four shorter and two longer bonds and can be regarded as reflecting a tendency towards four-coordination.

There is no doubt concerning the coordination number for copper in Cu_3WO_6 . The distances to the five nearest oxygen atoms are within 2.25 Å while the sixth oxygen is 3.10 Å remote. The details of the coordination figure should be evident from Table 5 and Fig. 2. It is seen that the deviation from regularity is predominantly a relaxation of the trigonal symmetry giving rise to one short and two long edges in the equatorial plane.

The most common coordination around bivalent copper seems to be the four-fold, square planar arrangement with or without two more distant ligands completing a distorted octahedron. Five-fold coordination has also been observed in a number of structures, especially of metal-organic compounds. In most of these latter cases the coordination figure is best described as a square pyramid but in a few struc-

tures, including the present one, it must be regarded as a triangular bipyramid. These are $\text{Cu}_2(\text{OH})\text{AsO}_4$ (olivenite)¹³ and the isomorphous $\text{Cu}_2(\text{OH})\text{PO}_4$ (libethenite)¹⁴, $\text{Cu}_2\text{O}(\text{SO}_4)$ (dolerophanite)¹⁵, $[\text{Cr}(\text{NH}_3)_6] \text{CuCl}_5$ ¹⁶ and μ_4 -oxohexa- μ -chlorotetrakis(triphenylphosphine oxide) copper(II)¹⁷. In the first three only one half of the copper atoms are five-coordinated, the other half of them have 4+2 neighbours.

The shortest distance between copper atoms is that between the atoms situated in two bipyramids that share an edge, i.e. the distance between adjacent copper atoms in the rings. This distance, 2.990 (+3) Å, may be compared with the closest approach of metal atoms in CuO, where the three shortest distances are 2.9005 (+3), 3.0830 (+3) and 3.1734 (+4) Å according to a recent refinement¹⁸. The present value, which occur twice for each copper atom, is seen to be almost exactly the mean of the two shortest distances in CuO. Corresponding distances in CuWO_{4-x} are 2.982 (+4) Å and 3.152 (+4) Å.¹⁹

The oxygen-oxygen distances are quite normal throughout. A shortening of the O-O distances along edges which are common to two polyhedra is a generally observed phenomenon in structures where there is no appreciable metal-metal interaction across these edges. This effect is noticeable also in this structure as the shortest edges within each polyhedron are those shared with other polyhedra. It is less pronounced for edges shared between two CuO_5 bipyramids than for those shared between a bipyramid and a WO_6 octahedron in accordance with the rules developed by Pauling from simple electrostatic arguments.

The "oxygen volume", $V_{\text{cell}}/n_{\text{O}}$, is 19.57 Å³ which indicates that the oxygen lattice is a fairly open one. Corresponding values for structures with small cations in a close packed oxygen framework usually lie within the range 16.0 - 16.5 Å³. The same thing is evident from the fact that the oxygen atoms have only nine oxygen near neighbours, lying within a distance of 3.10 and 2.92 Å, whereas the next nearest neighbours are not closer than 3.93 and 3.77 Å for O(1) and O(2), respectively.

This compound, which has crystallographically equivalent copper atoms in a somewhat unusual coordination with oxygen, should be studied by other methods, and investigations of its electric and magnetic pro-

perties have been started at this institute. In this connection a closer examination of possible non-stoichiometry will also be made. Preliminary measurements indicate that Cu_3WO_6 exhibits temperature independent paramagnetism over the temperature range 120-290°K with the value $\lambda_g \approx 4.5 \times 10^{-6}$ cgs units.²⁰

Acknowledgements. This investigation has been financially supported in part by the Swedish Natural Science Research Council and in part by the European Research Office, United States Army, Frankfurt am Main, Germany. Permission for the use of the computers was granted by the Computer Division of the National Swedish Rationalization Agency.

REFERENCES

1. Van Uitert, L.G., Rubin, J.J. and Bonner, W.A. J. Am. Ceramic Soc. 46 (1963) 512.
2. Clark, G.M. and Doyle, W.P. Spectrochim. Acta 22 (1966) 1441.
3. Conroy, L.E. and Sienko, M.J. J. Am. Chem. Soc. 79 (1957) 4048.
4. Sienko, M.J. and Weller, P.F. Inorg. Chem. 1 (1962) 324.
5. Gebert, E. and Kihlberg, L. Acta Chem. Scand. 21 (1967) 2575.
6. Hambling, P.G. Acta Cryst. 6 (1953) 98.
7. Cromer, D.T. and Waber, J.T. Acta Cryst. 18 (1965) 104.
8. Hanson, H.P., Herman, F., Lea, J.D. and Skillman, S. Acta Cryst. 17 (1964) 1040.
9. Cromer, D.T. Acta Cryst. 18 (1965) 17.
10. Steward, E.G. and Rooksby, H.P. Acta Cryst. 4 (1951) 503.
11. Keeling, Jr., R.O. Acta Cryst. 10 (1957) 209.
12. Chichagov, A.P., Ilyukhin, V.V. and Belov, N.V. Dokl. Akad. Nauk SSSR 166 (1966) 87.
13. Heritsch, H. Z. Krist. 99 (1938) 466.
14. Walitzi, E.M. Mineral. Petrogr. Mitt. 8 (1963) 614.
15. Flügel-Kahler, E. Acta Cryst. 16 (1963) 1009.
16. Mori, M., Saito, Y. and Watanabe, T. Bull. Chem. Soc. Japan 34 (1961) 295.
17. Bertrand, J.A. Inorg. Chem. 6 (1967) 495.
18. Norrby, L.-J. and Åsbrink, S. To be published.
19. Kihlberg, L. and Gebert, E. To be published.
20. Barvling, G. and Kihlberg, L. To be published.

Table 1. X-ray powder pattern of Cu_3WO_6 . The values for the intensity of the lines have been obtained from rough visual estimation putting very strong = 10 and very faint = 1. $\lambda = 1.54051 \text{ \AA}$.

$\Delta = \sin^2\theta_{\text{obs}} - \sin^2\theta_{\text{calc}}$. $\sin^2\theta_{\text{calc}}$ based on $a = 9.7989(\pm 2) \text{ \AA}$ calculated by least squares refinement.

<u>I</u>	<u>$h^2+k^2+l^2$</u>	<u>d_{obs}</u>	<u>$\sin^2\theta_{\text{obs}}$ $\times 10^5$</u>	<u>Δ $\times 10^5$</u>
9	3	5.660	1852	-1
4	4	4.898	2473	1
10	5	4.385	3086	-3
6	6	3.998	3711	3
4	8	3.455	4971	27
4	9	3.265	5566	4
6	11	2.954	6798	1
10	13	2.7199	8020	-12
10	14	2.6206	8639	-11
8	16	2.4496	9887	0
4	17	2.3766	10504	0
6	18	2.3096	11122	0
6	20	2.1906	12363	5
4	21	2.1384	12975	0
6	22	2.0900	13582	-11
3	25	1.9595	15451	3
2	26	1.9208	16081	15
6	27	1.8850	16697	13
10	29	1.8194	17924	4
5	30	1.7888	18542	5
6	32	1.7317	19784	11
1	33	1.7057	20391	0
8	35	1.6562	21630	3
6	36	1.6323	22267	22
6	37	1.6105	22874	11
9	38	1.5895	23482	1

V:11

<u>I</u>	<u>h</u> ² + <u>k</u> ² + <u>l</u> ²	<u>d</u> _{obs}	$\sin^2\theta$ $\times 10^5$ _{obs}	Δ $\times 10^5$
4	40	1.5494	24713	-2
8	41	1.5307	25320	-13
4	42	1.5119	25954	2
9	45	1.4614	27780	-25
9	46	1.4454	28399	-24
2	48	1.4140	29672	12
5	49	1.3998	30274	-2
5	51	1.3725	31494	-18
5	52	1.3590	32124	-6
5	53	1.3462	32739	-9
9	54	1.3337	33352	-14
4	56	1.3098	34585	-17
4	57	1.2964	35193	-27
5	59	1.2756	36460	4
5	61	1.2546	37693	1
5	62	1.2444	38313	3
3	64	1.2248	39546	0
1	65	1.2149	40196	32
2	66	1.2062	40780	-1
1	67	1.1967	41426	26
2	68	1.1880	42037	20
5	69	1.1795	42644	9
5	70	1.1710	43263	10
3	73	1.1468	45110	3
3	74	1.1389	45739	14
3	75	1.1314	46344	1
8	77	1.1169	47556	-22
4	78	1.1098	48169	-26

Table 2. The crystal structure of Cu_3WO_6 .Space-group: $\text{Pa}\bar{3} - \frac{\text{T}_h^6$ Unit cell parameter: $a = 9.797$ (± 3) ÅUnit cell content: 8 Cu_3WO_6

Atom	Position	\bar{x}	\bar{y}	\bar{z}	\bar{B}
W	8c	0.11703 (± 8)	0.11703 (± 8)	0.11703 (± 8)	0.19 (± 6)
Cu	24d	0.40443 (± 28)	0.24568 (± 26)	0.13762 (± 24)	0.69 (± 6)
O(1)	24d	0.2193 (± 13)	0.3016 (± 12)	0.0891 (± 12)	-0.13 (± 19)
O(2)	24d	0.4446 (± 15)	0.4636 (± 16)	0.1953 (± 16)	0.33 (± 24)

The errors given are the calculated single sigma values.

Table 3. Weight analysis obtained in the last cycle of refinement.
 $\Delta = ||F_{\text{obs}}| - |F_{\text{calc}}||$, w = weighting factor. The $w\Delta^2$ values have been normalized.

Interval sin θ	Number of independent reflections	$\overline{w\Delta^2}$	Interval $ F_{\text{obs}} $	Number of independent reflections	$\overline{w\Delta^2}$
0.000 - 0.209	24	1.411	0.0 - 57.2	20	1.707
0.209 - 0.263	22	0.502	57.2 - 72.7	20	0.943
0.263 - 0.301	22	0.732	72.7 - 89.1	21	1.167
0.301 - 0.332	24	1.160	89.1 - 102.1	20	0.638
0.332 - 0.357	20	1.213	102.1 - 119.2	21	0.926
0.357 - 0.379	24	1.044	119.2 - 135.7	20	0.409
0.379 - 0.400	20	1.290	135.7 - 154.4	20	0.738
0.400 - 0.418	13	0.661	154.4 - 178.8	21	1.079
0.418 - 0.434	21	1.216	178.8 - 205.1	20	0.944
0.434 - 0.450	13	0.769	205.1 - 260.2	21	1.449

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
0	0	0	150.4	142.2	5	5	1	221.4	232.0	7	8	2	243.9	242.7
0	10	0	140.3	120.9	5	6	1	178.9	186.6	8	3	2	73.4	77.2
0	12	0	184.5	193.7	5	7	1	134.1	132.8	8	4	2	65.9	64.8
2	2	0	88.5	81.2	5	8	1	193.2	190.0	9	4	2	98.7	87.1
2	4	0	217.4	231.4	5	10	1	138.4	145.0	9	5	2	103.5	103.2
2	6	0	72.7	75.4	5	12	1	207.0	222.5	9	7	2	161.0	161.4
2	8	0	42.0	57.3	6	3	1	156.2	151.9	11	5	2	60.2	55.6
2	10	0	137.8	135.3	6	4	1	105.8	104.1	11	4	3	33.4	25.6
2	12	0	112.4	114.6	6	5	1	133.1	124.4	11	3	3	119.5	114.8
4	4	0	230.4	242.5	6	6	1	111.9	109.0	11	2	3	102.1	100.7
4	6	0	159.7	155.9	6	7	1	43.7	45.9	11	1	3	193.0	204.4
4	8	0	191.4	207.5	6	8	1	135.4	143.9	13	4	3	82.4	77.6
4	10	0	260.3	283.6	6	10	1	99.4	99.4	13	3	3	109.0	108.9
4	12	0	147.3	150.2	6	12	1	163.7	154.6	13	2	3	133.4	141.5
6	4	0	202.3	198.8	7	3	1	122.7	123.3	14	4	3	183.9	204.7
6	6	0	20.0	27.0	7	4	1	57.2	47.7	14	3	3	204.2	224.8
6	8	0	224.9	244.4	7	5	1	89.0	75.7	14	2	3	51.6	48.5
6	10	0	109.4	104.7	7	6	1	141.4	136.4	14	1	3	27.8	26.9
6	12	0	143.1	150.3	7	7	1	123.4	110.1	14	0	3	127.8	131.2
8	4	0	178.6	180.5	7	8	1	142.1	134.9	15	5	3	190.4	205.3
8	6	0	113.2	102.9	7	10	1	142.1	134.9	15	4	3	120.5	113.6
8	8	0	250.4	249.1	7	12	1	193.3	191.4	15	3	3	89.4	90.1
8	10	0	96.7	88.3	8	3	1	88.3	87.3	15	2	3	117.4	109.0
8	12	0	41.4	55.6	8	4	1	141.9	132.4	15	1	3	117.4	109.0
10	4	0	121.9	129.6	8	5	1	183.0	189.6	15	0	3	255.7	265.1
10	6	0	138.8	130.4	8	6	1	111.6	94.0	15	5	3	142.4	155.7
10	8	0	107.4	105.1	8	8	1	110.9	102.1	15	4	3	223.9	244.4
12	2	0	104.4	94.3	9	3	1	194.7	215.3	16	6	3	119.2	118.0
12	4	0	154.5	157.4	9	5	1	101.8	94.6	16	5	3	70.0	68.2
12	6	0	147.7	174.1	9	7	1	134.1	139.8	16	4	3	72.5	64.0
12	8	0	147.5	174.1	10	3	1	100.7	93.3	16	3	3	142.2	139.2
12	10	0	192.5	201.4	10	4	1	84.4	86.2	16	2	3	89.2	82.0
12	12	0	104.5	99.2	10	5	1	127.4	121.7	16	1	3	51.0	54.2
14	2	0	101.5	94.4	10	6	1	48.5	57.0	16	0	3	93.1	91.7
14	4	0	124.5	121.0	10	8	1	109.4	117.6	16	5	3	81.5	69.2
14	6	0	153.1	150.9	10	10	1	81.5	74.4	16	4	3	98.9	101.9
14	8	0	94.4	84.6	12	2	1	11.8	4.3	16	3	3	122.9	118.6
14	10	0	96.4	101.4	12	4	1	8.0	5.4	16	2	3	144.8	159.2
14	12	0	63.2	59.3	12	5	1	69.7	74.2	16	1	3	80.5	77.9
16	2	0	132.2	135.9	2	2	2	75.7	67.1	10	0	6	47.5	43.6
16	4	0	43.8	34.5	2	3	2	115.4	104.0	10	5	4	230.0	254.9
16	6	0	79.7	74.5	2	4	2	71.3	69.0	10	4	4	47.5	43.6
16	8	0	65.2	44.4	2	5	2	203.4	244.7	10	3	4	34.4	34.5
16	10	0	175.4	197.5	3	3	2	150.4	155.9	10	2	4	50.2	35.7
16	12	0	90.1	87.1	3	4	2	164.9	170.1	10	1	4	70.7	47.7
18	2	0	134.9	144.3	3	5	2	100.7	103.0	10	0	4	100.4	103.0
18	4	0	141.3	134.8	3	6	2	159.9	170.4	10	5	4	132.1	133.3
18	6	0	43.6	57.0	3	7	2	171.2	194.7	10	4	4	270.1	275.2
18	8	0	186.3	200.1	3	8	2	80.0	79.1	10	3	4	250.9	264.9
18	10	0	82.1	77.7	3	10	2	90.3	85.1	11	5	4	250.9	264.9
18	12	0	111.1	44.0	3	12	2	194.5	189.3	11	4	4	75.8	75.7
20	2	0	49.0	44.0	4	4	2	209.0	221.1	11	3	4	84.1	80.1
20	4	0	205.2	228.4	4	5	2	149.0	153.4	11	2	4	202.9	214.8
20	6	0	78.1	49.4	4	6	2	130.2	144.1	11	1	4	123.4	124.5
20	8	0	47.0	47.8	4	7	2	62.4	59.0	11	0	4	151.7	159.3
20	10	0	90.4	84.1	4	8	2	79.2	71.9	11	5	4	193.3	199.4
20	12	0	94.5	88.3	4	10	2	115.4	109.4	11	4	4	120.5	122.8
22	2	0	172.5	194.1	4	12	2	200.7	170.0	11	3	4	154.5	159.8
22	4	0	177.4	188.1	4	14	2	187.1	182.5	11	2	4	80.0	75.9

Table 4. Observed and calculated structure amplitudes for Cu₃WO₆. The strong reflections which were considered to suffer considerably from extinction and therefore were given zero weight are marked by an asterisk.

Table 5. Interatomic distances and angles in Cu_3WO_6

<u>Within octahedra</u>		Distance between the oxygen atoms		
W - O(2) (3x)	1.791 (<u>+16</u>) Å	O(1)-W-O(1) (3x)	76.1 (<u>+5</u>)°	2.57 (<u>+2</u>) Å
- O(1) (3x)	2.085 (<u>+12</u>)	O(1)-W-O(2) (3x)	88.6 (<u>+6</u>)	2.72 (<u>+2</u>)
		O(1)-W-O(2) (3x)	89.3 (<u>+6</u>)	2.73 (<u>+2</u>)
		O(2)-W-O(2) (3x)	102.7 (<u>+6</u>)	2.80 (<u>+2</u>)
		O(1)-W-O(2) (3x)	161.0 (<u>+6</u>)	3.82 (<u>+2</u>)
<u>Within bipyramids</u>				
Cu - O(1b)	1.921 (<u>+12</u>) Å	O(1c)-Cu-O(1a)	81.1 (<u>+7</u>)°	2.57 (<u>+2</u>) Å
- O(1c)	1.953 (<u>+13</u>)	O(1c)-Cu-O(2b)	87.7 (<u>+6</u>)	2.78 (<u>+2</u>)
- O(1a)	2.002 (<u>+12</u>)	O(1c)-Cu-O(2a)	87.5 (<u>+5</u>)	2.91 (<u>+2</u>)
- O(2b)	2.060 (<u>+15</u>)	O(1b)-Cu-O(1a)	104.3 (<u>+3</u>)	3.10 (<u>+2</u>)
- O(2a)	2.243 (<u>+16</u>)	O(1b)-Cu-O(2b)	93.3 (<u>+6</u>)	2.90 (<u>+2</u>)
		O(1b)-Cu-O(2a)	83.4 (<u>+5</u>)	2.78 (<u>+2</u>)
		O(1a)-Cu-O(2a)	135.8 (<u>+6</u>)	3.93 (<u>+2</u>)
		O(1a)-Cu-O(2b)	136.3 (<u>+6</u>)	3.77 (<u>+2</u>)
		O(2a)-Cu-O(2b)	85.1 (<u>+8</u>)	2.91 (<u>+2</u>)
		O(1b)-Cu-O(1c)	170.8 (<u>+5</u>)	3.86 (<u>+2</u>)
<u>Between polyhedra</u>				
W - W	3.970 (<u>+1</u>) Å	O(1) - Cu	1.921 (<u>+12</u>) Å	
- Cu (3x)	3.090 (<u>+3</u>)	- Cu	1.953 (<u>+13</u>)	
- Cu (3x)	3.420 (<u>+3</u>)	- Cu	2.002 (<u>+12</u>)	
- Cu (3x)	3.516 (<u>+3</u>)	- W	2.085 (<u>+12</u>)	
- Cu (3x)	3.648 (<u>+3</u>)			
		O(2) - W	1.791 (<u>+16</u>)	
Cu - W	3.090 (<u>+3</u>)	- Cu	2.060 (<u>+15</u>)	
- W	3.420 (<u>+3</u>)	- Cu	2.243 (<u>+16</u>)	
- W	3.516 (<u>+3</u>)			
- W	3.648 (<u>+3</u>)			
- Cu (2x)	2.990 (<u>+3</u>)			
- Cu (2x)	3.219 (<u>+4</u>)			
- Cu (2x)	3.529 (<u>+3</u>)			

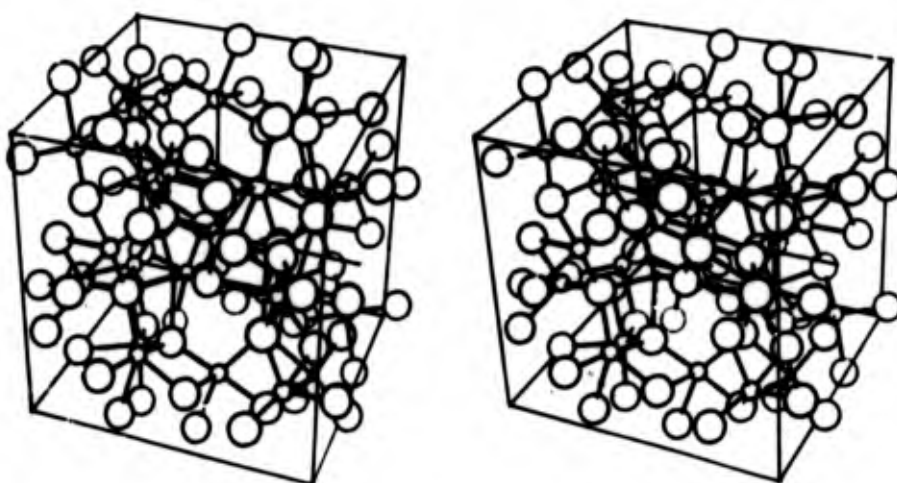


Figure 1. A stereo pair showing the Cu_3WO_6 structure. The metal atoms within one unit cell volume and their coordinating oxygen atoms are shown. The origin 0,0,0 is at the centre of the cube but is hidden behind an oxygen atom. The positive directions of the axes from this point are indicated forming a right-handed coordinate system with z vertical. Small spheres = W, medium spheres = Cu, large spheres = O atoms.

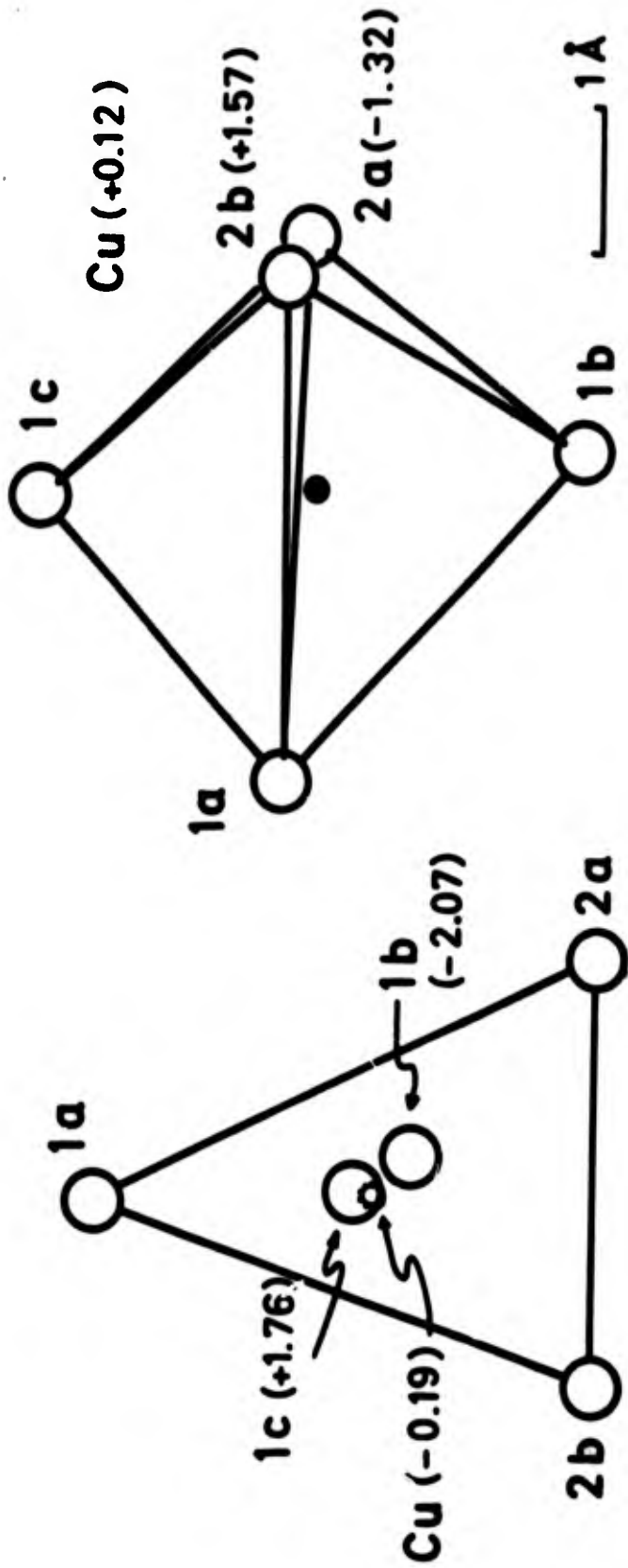


FIG. 2. The coordination of oxygen atoms around copper shown in two different projections. Left: Projection on the "equator" plane containing the oxygen atoms 1_a, 2_a and 2_b. Right: Projection on the plane through 1_a and the "poles" 1_b and 1_c. The values within parentheses are the distance in Å of the atoms above (+) or below (-) these planes.

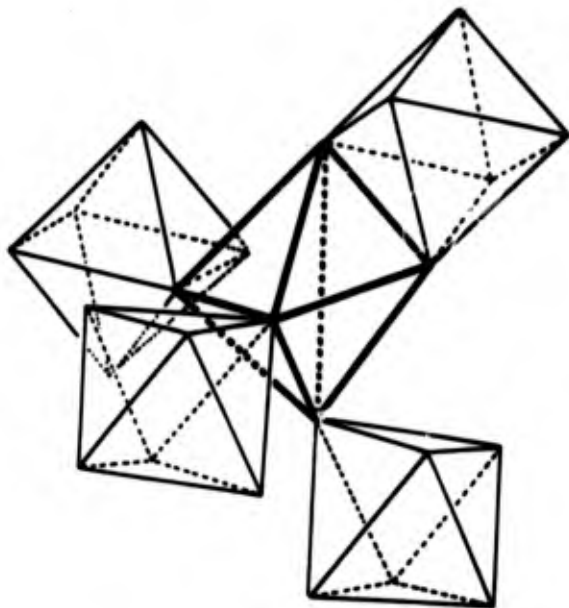


Figure 3 a. The arrangement of WO_6 octahedra around one CuO_5 triangular bipyramid.

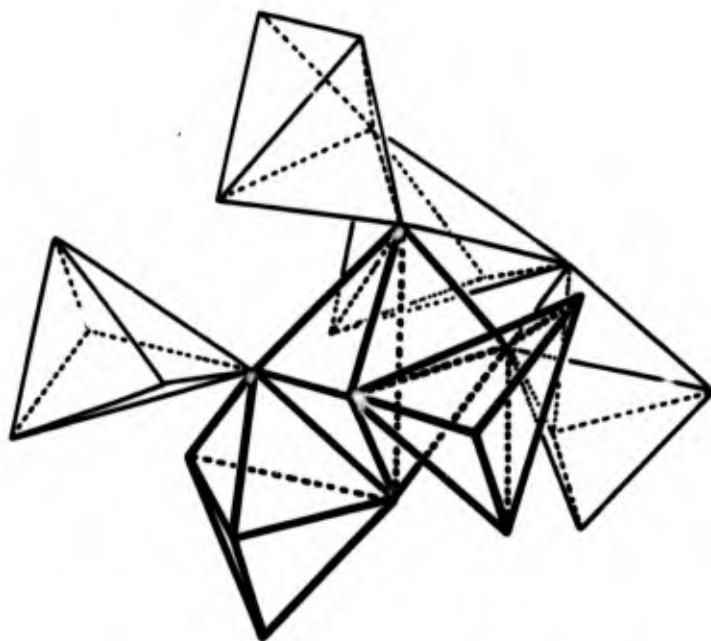


Figure 3 b. The arrangement of CuO_5 bipyramids around the same CuO_5 group as in Figure 3a. The two bipyramids which belong to the same bipyramid ring as the central one are also indicated by heavy lines.

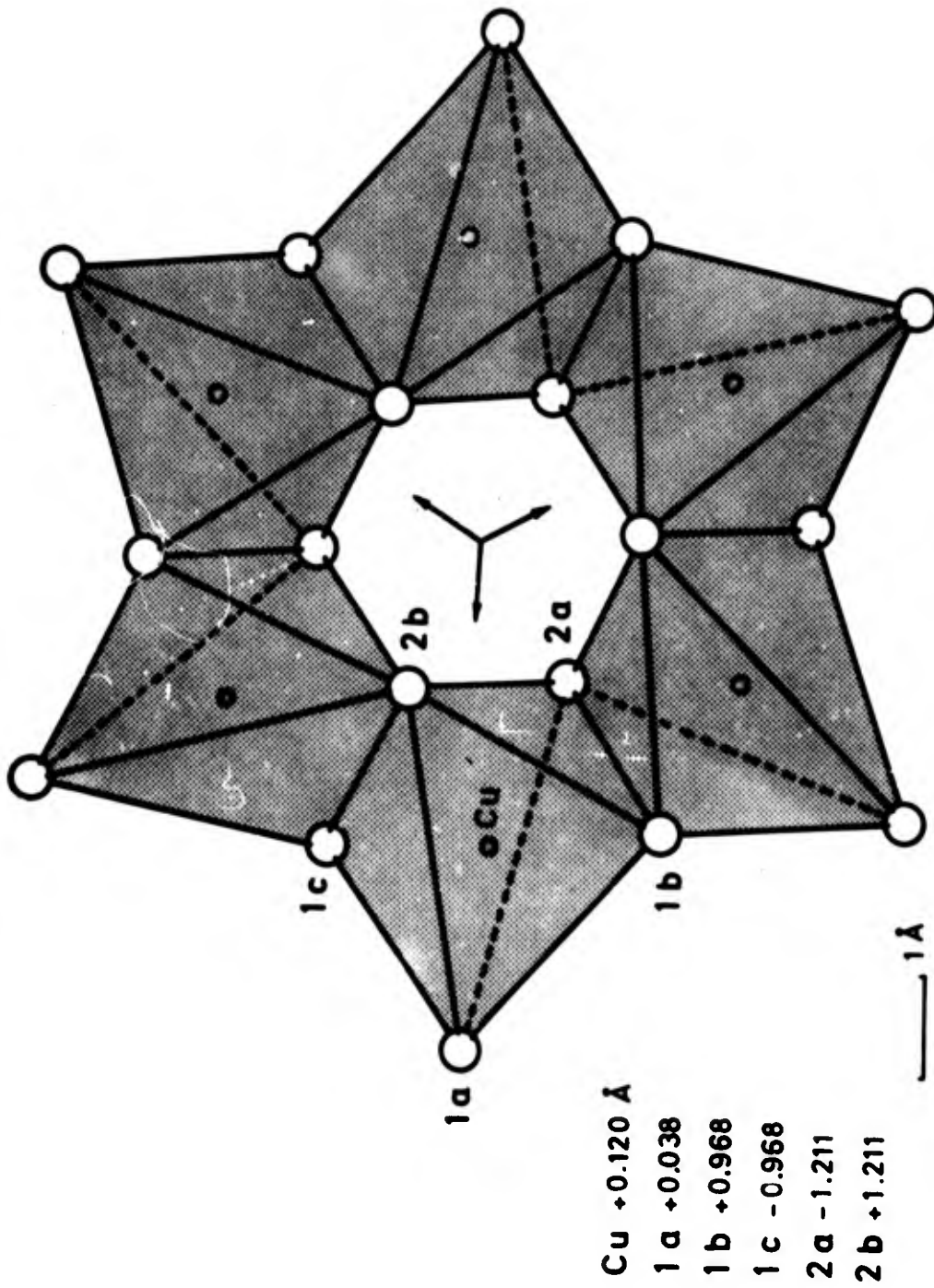


Figure 4. The arrangement of six CuO_5 triangular bipyramids forming a ring of symmetry $\bar{3}$ viewed along the trigonal axis. To the left are given the level of the indicated atoms above (+) or below (-) the plane through the inversion centre.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) University of Stockholm Institute of Inorganic and Physical Chemistry Stockholm, Sweden		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE Studies on Structural Relations in Crystalline and Vitreous Compounds			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Technical Report March 67 - March 68			
5. AUTHOR(S) (First name, middle initial, last name) Peder Kierkegaard, et al.			
6. REPORT DATE March 1968		7a. TOTAL NO. OF PAGES 150	7b. NO. OF REFS 39
8a. CONTRACT OR GRANT NO. DAJA37-67-C-0421		14. ORIGINATOR'S REPORT NUMBER(S)	
b. PROJECT NO.			
c. DA Accession No. 9320		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. DISTRIBUTION STATEMENT Distribution of this document is unlimited			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY US Army R&D Group (Europe) APO New York 09757	
13. ABSTRACT Studies on the structural properties of crystalline and vitreous polymolybdates and polywolframates have been performed. Results obtained from X-ray studies on sodium dimolybdate and diwolframate are reported and discussed. Details of the structural investigation of dipotassium tetrwolframate are given. The research work has also comprised some studies on glasses and crystalline substances on arsenate molybdate (wolframate) basis containing alkali or silver atoms. Structural data are given for the crystalline compounds $\text{NaZr}_2(\text{PO}_4)_3$ and $\text{U}(\text{PO}_3)_4$. Studies on the structural conditions in the ternary oxide systems containing vanadium and molybdenum or wolfram have been performed. Description of the structures are given for the crystalline phases $(\text{Mo}_{0.93}\text{V}_{0.07})_5\text{O}_{14}$, $\text{W}_{0.375}\text{V}_{0.625}\text{O}_{2.5}$ and $\text{W}_{0.35}\text{O}_{0.65}\text{O}_{2.5}$. Preliminary results are given for investigations of copper wolfram oxides. X-ray investigations have been performed on the compounds CuWO_{4-x} and Cu_3WO_6 . The preparation and properties of amorphous molybdenum trioxide are described. A summary of the types of calculations carried out by computer within this research project is given. Apparatus and measuring techniques for studies of magnetic susceptibility of vitreous and crystalline specimens have been developed. Measurements over the temperature region 90°K-298°K have been performed on the crystalline compounds MoPO_4 and $\text{W}_2\text{O}_3(\text{PO}_4)_2$ and glasses prepared from these phases. The crystals of MoPO_4 have been found to be paramagnetic while the other compounds are diamagnetic.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Ceramics						
Crystalline Compounds						
Vitreous Compounds						
X-ray Diffraction						