Installation Program for S-FAC, and Review of Research Activities in X-Ray and Solid State Laboratory, Department of Physics, The Pennsylvania State College, June 4 - 5, 1952.

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R. Pepinsky

R. Pepinsky
Research Professor of Physics
June 7, 1952.

Installation of S-FAC, and Review of X-Ray and Solid State Laboratory Research

Rooms 117, 5 and 6, Osmond Laboratory
Department of Physics
The Pennsylvania State College
June 4-5, 1952.

Wednesday, June 4:

11:00 A.M. Room 117, Osmond Laboratory

(1) Introductory Remarks and Survey of Activities: R. Pepinsky.

2:00 P.M. Room 117, Osmond Laboratory

(2) Completion of Survey and Introduction to Biochemical Program: R. Pepinsky.

(3) Biochemicals, Selection and Preparation: W. G. and G. Overend.

(4) Terramycin and Aureomycin: T. Watenabe and T. Doyne.

(5) Podophyllotoxin: W. G. Perdok.

(6) Jervine: R. Collin

(7) Pyridyl Antihistamines: J. Rathlev.

(8) Castoramine: K. Ericks.

(9) Dicyclopentadiene Iron: P. F. Eiland

(10) Geiger Counter Spectrometer: P. F. Eiland

4:00 P.M. Rooms 5 and 6, Osmond Laboratory.
<u>Laboratory Tour and Discussions.</u>

Demonstrations of X-ray equipment, chemistry and microscopic laboratories, low-temperature X-ray laboratory, micro-beam X-ray tubes.

7:30 P.M. Buffet Dinner, Autoport Terrace.
($2.00 per person).

9:00 P.M. Dance, Autoport
($1.25 per couple).

Thursday, June 5.

9:30 A.M. Room 6, Osmond Laboratory.

Demonstration of X-RAC and S-FAC.

11:00 A.M. Room 117, Osmond Laboratory.

(11) Facsimile Recording: A. Moodie and T. Noguchi

(12) Discussion of Use of X-RAC and S-FAC: R. Pepinsky

2:00 P.M. Room 117, Osmond Laboratory.

(13) Program on Crystal Transitions: R. Pepinsky

(14) Ferroelectricity in the Perovskites: G. Shirane

(15) Ilmenite Structures: A. Magneli

(16) Transitions in the Dihydrogen Phosphates and Arsenates: B. C. Frazer.

(17) The $NH_4H_2PO_4$ Transition: R. Keeling

(18) $LiNH_4$ Tartrate$\cdot H_2O$: R. Vernon

(19) $NH_4PO_3\cdot 6H_2O$: K. Drenck

(20) Thermal Measurements: E. J. Rock and H. Danner

(21) Electromechanical Transducer Measurements: P. Tamarkin and W. Canty

(22) Theory of Ferroelectric Activity: G. Barsch

4:00 P.M. Rooms 5 and 6, Osmond Laboratory

Demonstrations of crystal growth equipment, dielectric, piezoelectric, thermal and electromechanical transducer measurements.

Remarks on the Occasion of
the Installation of S-FAC.

During each of the first two years of the three since our X-ray program was initiated at Penn State - succeeding that of Professor Wheeler Davey who founded and gave a high reputation to work in the X-ray field in this College - we held a little meeting here with some of our colleagues in the world of X-ray analysis, to discuss aspects of the state of our science, and to review at the same time the activities of our own laboratory. This present meeting, which you grace with your presence, is in part a continuance of this custom. This year we have felt the need for something more than this, however. A university is a collection of scholars - not, as is engraved on every university library (ours not excepted) a collection of books; and the strength of a university depends as much upon the sharing of scholarship and of ideas as it does upon the individual competence of its faculty. We are fortunate to have certain strong scientific bonds with our Penn State colleagues in chemistry, mineral sciences, engineering and mathematics. We have strong interests in other fields of knowledge and scholarship, however, even though our interests are certainly non-professional; and we treasure the thought that some of our fellows on the faculty, scientists and non-scientists alike, and even members of that Elysian class, our administrators, would like to gain a closer view of what goes on in our minds and our laboratories.

It is for this reason that we have invited to the present discussions and demonstrations a good number of non-crystallographers and non-physicists of this campus. We shall not talk down to you. X-ray crystal analysis is an esoteric activity at best. We utilize X-rays, which no one can see, to trace the positions of electrons, atoms and molecules - which no one can see also - in solids. But we want to tell you why we do this, and how, and what our results might mean. We want to show you a team of investigators, at work on a closely-knit plexus of problems, with fine modern tools and techniques. And we want to show you how our students are trained, directly in the frontier problems of science, and what they are accomplishing during this training. So for two days we shall be carrying on a sort of five-ring circus. We will try to show the non-scientists among you what we are concerned with as scientists, how we approach these problems, how our research is organized, and what our tools - and ourselves - look like. We will try to show our colleagues who are chemists, engineers, mineralogists, biologists, and so on, how our methods can aid in the solution of their own problems. We will discuss and demonstrate our program and procedures for student training. We will review and discuss our specific activities in X-ray analysis and solid state physics with the experts in these fields who have so kindly joined us for this occasion. We will introduce you all to the several foreign visitors in our group, of whose participation in our program we are particularly proud. And we will attempt to express our gratitude to both The Pennsylvania State College and the various outside agencies which have provided support for our work.

S-FAC: A New Tool in X-Ray Analysis.

The excuse for this gathering is the placing in operation of a new tool in X-ray analysis — our computer S-FAC. The name, like a railroad timetable, is meant to be read backwards:*

C = computer

A = analogue

S-F = structure-factor.

This classifies S-FAC as a machine which calculates how a given structure of atoms will scatter X-rays; and it indicates that the machine simulates a calculation, instead of actually performing it with numbers.

S-FAC is one of two computers in our laboratory. It is actually a little brother to X-RAC, our machine for calculating atomic arrangements in crystals from X-ray scattering measurements. These two machines operate so rapidly, and are so matched to the information which is available to us from our experimental measurements and the information which our minds can utilize, that they permit us to conserve a maximum amount of our time and mental powers for *thinking*, rather than wasting these on computational drudgery.

S-FAC and X-RAC are machines which could not have been built in a university a dozen years ago. They represent the fruit of *organized* research, combining the mind and competence of investigators from several different scientific disciplines; and, more important in a practical sense, they represent the fruit of organized *support* for such research.

Among the aims of this gathering is further public acknowledgement of the very great gratitude we feel toward the Office of Naval

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* I owe this joke to Mr. Morse, our provost.

Research, which has provided contract funds for the construction, operation, utilization and further development of our computers. The Office of Naval Research is represented here today by Dr. Nelson M. Blachman of the Mathematical Sciences Division, Computer Branch, and by Dr. A. W. Pryce of the Physics Branch. We are not only happy to have another opportunity to express our appreciation of the support which the Office of Naval Research has given us, but we are grateful for the visit of these two representatives.

Low-Temperature Research.

As we discuss various aspects of our activities, you will observe that about half of our crystal structural studies are directed at elucidation of molecular configurations of biochemical compounds of medical importance, and the rest are concerned with more fundamental problems of interatomic bonding and crystal transitions. In the latter problems we find it necessary to make measurements over very wide temperature ranges. The most interesting and revealing studies are those at very low temperatures — as close as possible to absolute zero. We are pleased to be able to show you a machine which we have recently acquired for the production of these extremely low temperatures. This is our Collins Cryostat for liquid helium production.

Our low-temperature program is supported to a large extent by the Air Research and Development Command, under a contract issued from the Wright Air Development Center. We are very pleased to have Mr. William M. Schofield here, representing that agency, to review the work which we are conducting under Air Force support; and we are delighted to be able to acknowledge that support. Helium gas for liquifaction is supplied to us by the Office of Naval Research.

You will see, among other things, the beautiful low-temperature X-ray camera which has been constructed by our School of Chemistry and Physics Shop. This camera has been constructed under our contract with the Signal Corps Engineering Laboratories.

Other Acknowledgements of Support.

In the survey of research activities with which you have been provided, acknowledgement is made of support from a number of other organizations. We have taken great pride in grants from the Rockefeller Foundation, the Research Corporation, the Eli Lilly Company, Charles Pfizer and Co., the DuPont company, and the Gulf Research Laboratory, for support of our biochemical studies. The Office of Naval Research has also supported these studies. Our electromechanical transducer program is supported also by the Office of Naval Research.

Our fine laboratories are in themselves clear evidence of our vast debt to the College administration. (Diagrams of the laboratory layouts are included in the Survey). We expect soon to be able to move almost all X-ray equipment into room 7, adjacent to our present space; and completion of this arrangement will provide us with the finest physical facilities I have seen anywhere.

Visiting Crystallographers.

We have two categories of visitors with us, who are actively engaged in crystallographic research. The first group I will introduce to you are friends who are here just for the meeting today and tomorrow. These are, in alphabetical order:

Prof. Joseph D.H. and Dr. Gabrielle Donnay, from The John Hopkins University, Department of Geology and Chemistry.

Dr. David Harker, director of the Protein Project, at the Polytechnic Institute of Brooklyn.

Dr. Jerome and Dr. Isabella Karle, from the Naval Research Laboratory in Washington.

Dr. John Kasper, from the General Electric Research Laboratories in Schenectady.

Dr. A. L. and Dr. Elizabeth Patterson, from the Institute for Cancer Research, Lankenau Hospital, Philadelphia.

We have already acknowledged the presence of Dr. A. W. Pryce and Dr. Nelson M. Blachman of the Office of Naval Research, and Mr. William Schofield of the Wright Air Development Center.

The second group of visitors call other laboratories their homes, but they are here with us on extended stays from several months to two or more years. I will list these in the order of their appearance in our Survey.

Dr. Alexander Moodie, from the Australian Commonwealth Scientific and Industrial Research Organization in Melbourne. Dr. Moodie is here to learn about the construction and inner workings of X-RAC and S-FAC, in order that similar machines can be constructed in Australia.

He has been in charge of the construction of the facsimile recorder for the computers, in addition to his other activities; and he is an indispensable member of the Penn State cricket team.

Mr. Teruo Noguchi, from Osaka University in Japan. Mr. Noguchi is an experienced electronic circuit designer. He is working with Dr. Moodie on the facsimile recorder, and is aiding as well in X-ray photon counter system design.

Prof. Alberto Calderon, from Argentina, and now at Ohio State University, is a consultant on our theoretical program, a frequent visitor, and a close member of our group. He is also our chief instructor in the tango.

Prof. Kaj and Mrs. Karin Drenck, from Copenhagen. The Drencks are no longer considered visitors, and will ultimately become permanent members of our staff. Mrs. Drenck has been our chief editorial assistant, and has prepared for publication the reports of our first conference on <u>Computing Methods and the Phase Problem in X-Ray Analysis</u>; and Prof. Drenck has designed our fine-focus X-ray systems, directed construction of our latest photon counter circuits, directed the installation of our Collins cryostat, assisted in dielectric crystal measurements, and is now carrying out an X-ray analysis of ammonium metaphosphate.

Dr. Gen Shirane, from the Tokyo Institute of Technology, who is one of the leading research workers in solid state physics, and who is conducting dielectric, X-ray, thermal and mechanical measurements on crystals.

Mr. Eustace Edgerton Francis, from Jamaica. Mr. Francis is a graduate assistant in the dielectric measurements program. He is another of our cricket experts.

Prof. Wiepko G. Perdok, from the University of Groningen, Netherlands. Prof. Perdok is one of the world's leading crystal morphologists, and he is our encyclopedia and guide in all matters relating to external crystal measurements. He is also conducting an X-ray analysis of the important antimitotic agent podophyllotoxin.

Dr. Franco Jona will arrive in our laboratory the day after our meetings, from the Eidgenossische Technische Hochschule in Zurich, Switzerland. He will direct new instrumentation of our dielectric and mechanical crystal measurements.

Dr. Klaas Eriks and Mrs. Maartje Eriks, from the University of Amsterdam. Dr. Eriks is another of the very competent students of our dear friend Prof. Caroline MacGillavry of Amsterdam, the third such we have enjoyed in our group. He is at present analyzing the structure of a new biochemical, castoramine. Mrs. Eriks is assiting in the dielectric measuremetns program.

Mr. Gerhard Bersch is from the Technical University of Berlin, and his presence here is sponsored by the U.S. High Commissioner for Germany and the Department of State's Youth Activities Branch. He is our theoretical physicist, and has been carrying on studies of crystal transitions, the nature of ferroelectric activity in crystals, and some aspects of the phase problem in X-ray analysis.

Prof. Arne Magneli is our second visitor from Prof. Gunnar Hagg's great laboratory in Uppsala, Sweden. He is engaged in various inorganic structural studies connected with our ferroelectric research, particularly on members of the ilmenite group, and is the acknowledged expert in the structural chemistry of tungsten and molybdenum oxides.

Prof. Tokunosuke Watanabe is from Osaka University, Japan. We feel extremely fortunate in our association with Prof. Watanabe, one of the foremost X-ray analysts of his country, and Japan has been a leader in this scientific field. Prof. Watanabe is at present engaged in the very difficult analyses of terramycin and aureomycin; and he has completed a structural study of a halogenated methyl tropolone.

Prof. Octavio Cano-Corona, here on a Rockefeller Foundation fellowship from the University of Mexico, is working with Dr. Robert Collin on the structure of the important alkaloid jervine, and also assists in powder diffraction analyses.

Mr. Jørgen Rathlev, from the Technical University of Copenhagen, Denmark, is just completing an analysis of the structure of a pyridil antihistamine, and has conducted studies on α-lipoic acid, one of the B-group vitamines. Mr. Rathlev is an expert both in X-ray analysis and mountain climbing.

Prof. Gerhard Schmidt, of the Weissman Institute in Rehovoth, Israel, will join us, under a grant from the Rockefeller Foundation, at the end of the present month. Prof. Schmidt will undertake an analysis of cyclic polypeptide antibiotics, and particularly Gramicidin-S.

Dr. George Overend and Mrs. Gina Overend, from the laboratory of Prof. M. Stacey of the University of Birmingham, England, are here under our Rockefeller Foundation grant for biochemical research. They have guided our choice of biochemicals for X-ray analysis, and have prepared the proper crystalline derivatives for these studies. Preparation of proper crystals is the most important step in the X-ray studies, and our progress with the structural analyses of a good number of compounds is directly due to the efforts of these extremely able investigators.

Mr. Niels Olesen, from the Technical University of Copenhagen, Denmark, is now in charge of operation of the Collins cryostat and associated instrumentation. He will also assist in the instrumentation of our high-brilliance micro-focus X-ray tubes.

Other investigators from outside the country who are coming shortly are:

Mr. Jorge R. Cordero-Funas, an electronic engineer from Buenos Aires, Argentina;

Dr. R.V.G. Sundero-Rao, a solid-state physicist from Osmania University, Hyderabad, India;

Prof. Elysiaro Tavora, an outstanding X-ray analyst from the the Faculdade Nacional de Filosofia, Rio de Janeiro, Brazil;

Dr. Donald Smits, an X-ray analyst from the laboratory of Prof. Wiebenga in the University of Groningen, Netherlands.

Mr. Henri Diamant, an electronics engineer, trained at the Technical University of Copenhagen, Denmark.

Mrs. Tara Purshottam, from India, but trained in biochemistry At Penn State.

<u>Main Laboratory Staff</u>.

Visitors from outside the country comprise between 25 and 30% of our personnel. The large number of American staff members precludes my doing much more than referring you to the Survey for names and activities. The scientific group does include:

Dr. Elizabeth Rock, in charge of thermal measurements;

Professor Paul Tamarkin, in charge of electro-mechanical transducer measurements;

Dr. Robert Collin, conducting the X-ray analysis of the alkaloid [redacted] jervine;

Mr. Paul Jarmotz, our chief electronics designer; in charge of the computer construction program;

Mr. Benjamin Chalmers Frazer, and Mr. Rolland Keeling } on low temperature X-ray analyses and dielectric measurements.

Mr. Philip Frank Eiland, on biochemical structure analyses and Geiger counter spectrometer measurements;

Mrs. Beverly Brown, in charge of X-RAC and S-FAC computing;

Mr. Thomas Doyne, on the terramycin-aureomycin X-ray analysis;

Mr. Robert Vernon, on the $LiNH_4tartrate\cdot H_2O$ structure analysis;

Dr. Waldemar Scheyer
Mr. Edward Zemyan
Mr. Elliott Burrell
Mr. William Pavelich } on crystal synthesis;

Mr. Horace Damner, on thermal measurements;

Mr. William Canty, on the electromechanical transducer measurements;

Mr. Clifford McCarty
and Mr. John McLaughlin } on dielectric measurements;

I do not list here our fine group of electronics, machine shop, photographic, drafting, and general laboratory technicians. We have also - as you can readily see - a competent and long-suffering group of secretarial and office assistant.

Nineteen of our personnel are graduate students, some taking degrees at Penn State and others doing research here which will be applied toward higher degrees in other countries. Each student works directly under a competent senior investigator.

Concerning the Program for the Meeting.

This is our staff. Our intention is that you meet these people and have them explain their work to you. I would now like to tell you our specific plans for this meeting.

I will devote the remainder of this morning to a general review of the laboratory program, following the Survey prepared for you. We will return at 2 P.M. for a series of very short discussions of some of the work in progress, presented by the investigators involved; and we will then spend an hour or so in the laboratory, viewing this work in progress and providing you with opportunity for direct discussions with the investigators.

On Thursday morning we will view the computers, and then discuss procedures for their use. This will require the participation of our visitors. On Thursday afternoon we will continue presentations of specific research, and proceed then to additional direct discussions in the laboratory.

All of you will be aware of the dinner this evening, on the Terrace of the Autoport, at 7:30 P.M. This will be followed at 9:00 P.M. by a dance at the Autoport. We snatch at any opportunity to organize a dance, and this meeting was an obvious chance which we could scarcely resist. Mrs. Pepinsky and the Office Staff are responsible for these arrangements, which sound fairly interesting to me.

Our Provost, Mr. Morse, has agreed to make a few well-chosen remarks after the dinner; and I herewith warn our visiting crystallographers, and our Navy and Wright Field friends, that they may anticipate calls for similar service - similarly limited in extent, of course.

Survey of Research and Personnel under Direction
of Prof. Ray Pepinsky, X-Ray and Solid State Laboratory,
Department of Physics, The Pennsylvania State College, May 1, 1952.

R. Pepinsky

R. Pepinsky
Research Professor
of Physics

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Active Research Programs and Investigators under Direction of R. Pepinsky, Pennsylvania State College X-Ray and Solid State Laboratories, Department of Physics, May 1, 1952.

I. Electronic Computer Program, under Contract with Office of Naval Research.

A. Electronic Development and Operations:

Dr. R. Pepinsky, Research Professor: theory and design of X-RAC and S-FAC.
Paul Jarmotz, Research Associate: chief electronic designer.
Dr. Alexander F. Moodie, Research Associate: electronic designer and theoretician.
Teruo Noguchi, Research Assistant: electronic designer.
Jorge R. Cordero-Funas*, Research Assistant: electronic designer.

Charles Douds
Alan R. Gedance
Edward Greenberg
Mahlon S. Knott } electronic technicians.
Clifford G. Stebbins
M. Dean Underwood

Aside from maintenance and developmental changes of X-RAC, this group is now chiefly concerned with the completion and operation of S-FAC, the structure-factor computer, and with facsimile recording of X-RAC signals.

B. Computing Group.

Beverly R. Brown, Research Assistant: in charge of X-RAC computations.
P. Frank Eiland, Graduate Fellow: crystallographer.

Helen Clements
Sara A. Budinger } computers.
Richard Voigtsberger

Robert Ebeling } photographers.
Malcom Eckley

Virginia Jeffrey } photographic assistants.
Silvia Silver

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*Beginning July, 1952.

This group is concerned with the actual operation of X-RAC on crystal-structural problems, the computations of structure-factors for refinement of analyses, and the preparation and filing of all data. Some 5000 syntheses have been photographed since X-RAC was installed at Penn State, and the machine has assisted in approximately 150 structure analyses.

II. X-Ray Analysis Theoretical Program, under Contract with Office of Naval Research.

Dr. R. Pepinsky: theory of phase determination. (See also I A).
Dr. Alberto Calderon, Mathematical Consultant: Fourier theory.
Dr. Alexander F. Moodie, Research Associate: phase theory. (See also I A).

This group, which during the past two and a half years has also included Dr. Caroline H. MacGillavry, Dr. J. A. Goedkoop, Dr. William Cochrane and Dr. Edwin Akutowicz, has been concerned with alleviation of the phase difficulty in X-ray analysis. Two conferences on the theory of analyses have been held at Penn State, one in April, 1950 and the second in April, 1951. Several major papers have been prepared in the field from this laboratory, and a volume of papers from the 1950 conference will be published in June, 1952.

III. Solid State Program, under contracts with Signal Corps Engineering Laboratory, Office of Air Research, and Office of Naval Research.

A. Electrical, Mechanical, Optical and Thermal Measurements.

Dr. R. Pepinsky, Project Director: crystal physics and chemistry; equipment design. (See also I A, II.)

Dr. E. J. Rock, Research Associate: specific heat and entropy measurements; helium cryostat operation.

Horace Danner, Graduate Assistant: thermal measurements.

John Slezak, Technician: thermal measurements.

Kaj Drenck, Visiting Asst. Professor: in charge of helium cryostat operation.

James McCann, Technician: helium liquifier operation.

Dr. Gen Shirane, Research Associate: thermal and mechanical measurements.

Rolland Keeling, Research Assistant: dielectric and piezoelectric resonance measurements.

B. Chalmers Frazer, Graduate Fellow: dielectric measurements.

Eustace E. Francis, Graduate Assistant: dielectric measurements.

Clifford McCarty, Research Assistant: dielectric and piezoelectric measurements; crystal plating; equipment design.

John McLaughlin, Technician: dielectric measurements.

Dr. Paul Tamarkin, Asst. Professor: electromechanical transducer measurements; acoustical tank design.

William Canty, Graduate Assistant: electromechanical transducer measurements; electronic circuit design.

Carl Kircher, Technician: electronic construction for electromechanical measurements.

Dr. Wiepko G. Perdok, Research Associate: optical and microscopic measurements of crystals and crystal transitions.

Dr. Franco Jona[*], Research Associate: crystal elasticity measurements; general crystal physics.

Dr. R. V. G. Sundera-Rao[**], Research Associate: crystal elasticity measurements; general crystal physics.

Robert E. Newnham[**], Research Assistant: dielectric and piezoelectric measurements.

This group is concerned with electric, mechanical, optical and thermal measurements of crystals, for applications as ferroelectrics, high dielectrics, piezo-electric frequency-control elements, electromechanical transducers, etc. Physical measurements have been made on several hundred crystals, and several new ferroelectrics and high dielectrics have been discovered.

[*] Beginning June, 1952.

[**] Beginning September, 1952.

B. Crystal Preparation for Physical Measurements:

Dr. Waldemar Scheyer, Research Assistant: chemist; preparation of inorganic and organic crystals from solutions and gels.

Edward Zemyan, Research Assistant: chemist; preparation of crystals at high temperatures from solutions, and from vapor phase.

Maartje Eriks, Technician: crystal preparation and chemical analyses.

Dr. Franco Jona*, Research Associate: special crystal growth problems. (See also III A).

This group is concerned with the synthesis of compounds and the preparation of materials suitable for physical measurements.

C. Theoretical Studies.

Dr. R. Pepinsky, Research Professor: crystal chemistry; theory of crystal transitions. (See also I A, II, III A.)

Gerhard Barsch, Research Fellow: thermodynamic and electro-optical theoretical studies.

Dr. Paul Tamarkin, Ass't. Professor: theory of acoustical waves in solids. (See also III A).

Dr. Arne Mägneli, Research Associate: crystal chemistry.

Dr. Franco Jona*, Research Associate: theory of ferroelectric activity. (See also III A, B.)

This group is concerned with theoretical studies in crystal physics and crystal chemistry, and the nature of inter-atomic bonding and crystal transitions.

D. X-Ray Analysis of Crystal Transitions.

Dr. R. Pepinsky, Research Professor: theory and experimental design of X-ray analyses of crystal transitions. (See also I A, II, III A, C).

B. Chalmers Frazer, Research Fellow: low-temperature X-ray analysis of dihydrogen phosphate transitions. (See also III A.)

Robert C. Vernon, Graduate Assistant: X-ray analysis of $LiNH_4$tartrate$\cdot H_2O$.

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*Beginning June, 1952.

Rolland Keeling, Research Assistant: low-temperature X-ray analyses of ammonium transitions and dihydrogen phosphates. (See also III A.)

Kaj Drenck, Visiting Asst. Professor: X-ray analysis of ferroelectric ammonium metaphosphate. (See also III A.)

Dr. Tokunosuke Watanabe, Research Associate: X-ray analysis of complex halides and oxy-halides.

Dr. Gen Shirane, Research Associate: X-ray analysis of perovskite-type ferroelectrics and antiferroelectrics. (See also III A.)

Dr. Arne Mägneli, Research Associate: X-ray analysis of molybdenum oxide and tungsten oxide systems. (See also III C.)

Octavio Cano-Corona, Rockefeller Fellow: X-ray powder analyses of ferroelectric crystals.

Maartje Eriks, Technician: X-ray powder analyses. (See also III B.)

Teruo Noguchi, Research Assistant: X-ray analyses of crystal transitions; in charge of direct photon-counter measurements. (See also I A.)

Dr. Robert Collin, Research Associate: diffuse scattering of X-rays due to thermal vibrations in crystals.

Two or more graduate students will be added to this program in the Fall of 1952.

The X-ray group investigates the structural mechanisms of crystal transitions; high dielectric, piezoelectric and ferroelectric activity; thermal vibrations in crystals; crystal elasticity properties; and special problems in crystal chemistry. The ferroelectric transition of KH_2PO_4 has been fully analyzed; the structure of $LiNH_4$tartrate$\cdot H_2O$ above its Curie point has been determined; the structure of H_3PO_4 has been analyzed; and studies of perovskite and related close-packed oxygen network ferroelectrics and antiferroelectrics are in progress, as are studies of complex halides and oxy-halides, and of additional tartrates and phosphates.

IV. Biochemical Structure Program, under Contract with Office of Naval Research, and Grants and Fellowships from the Research Corporation, Rockefeller Foundation, Eli Lilly Research Laboratory, Charles Pfizer and Co., DuPont Co., and the Gulf Research Laboratory.

A. X-Ray Analyses.

Dr. R. Pepinsky, Research Professor: selection of compounds for analyses; direction of X-ray analyses and computational procedures. (See also I A, II, III.)

P. Frank Eiland, Research Fellow; assistant director of biochemical structure laboratory; structure analyses of fructose, isomycomycin, pentadienes, antibiotics. (See also I B).

Dr. Wiepko G. Perdok, Research Associate: X-ray analyses of podophyllotoxin haloacetates. (See also III A.)

Joergen Rathlev, Research Assistant: X-ray analyses of pyridil antihistamines and α-lipoic acid.

Dr. Tokunosuke Watanabe, Research Associate: X-ray analyses of aureomycin and terramycin salts. (See also III D.)

Thomas Doyne, Graduate Assistant: X-ray analysis of terramycin and aureomycin salts.

Dr. Robert Collin, Research Associate: X-ray analysis of jervine hydrohalides, vitamine B_{12} derivatives and fragments. (See also III D.)

Octavio Cano-Corona, Rockefeller Fellow: X-ray studies of jervine hydrohalides. (See also III D.)

Dr. Klaas Eriks, Research Associate: X-ray analyses of castoramine salts, thebaine and methylthebaine salts.

Dr. Gerhardt Schmidt*, Rockefeller Fellow: X-ray analyses of Gramicidin-S and synthetic polypeptides.

Dr. Elysiario Tavora**, Research Associate: X-ray analysis of the citrovorum factor.

Dr. Donald Smits**, Research Associate: X-ray analysis of fumagillin.

Two or more graduate students will be added to this program in

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*Beginning July 1, 1952.

**Beginning September, 1952.

the Fall of 1952. Completion of several of the problems listed above will permit attacks on additional compounds, including the structures of tropine and pseudotropine, gelsemine, coumingine, various polysaccharides, desoxyribonucleotides and -nucleosides, and new antibiotics.

This group is conducting X-ray analyses of the molecular configurations of organic substances of medical importance. The structures of ergine, colchicine, isomycomycin, tropolone methyl ether, pyridyl antihistamines, fructose and glutamine have been completely determined, and analyses of jervine, terramycin and aureomycin, podophyllotoxin and several other compounds are nearing completion.

In general, the biochemical studies are concerned with structural problems which have not responded to usual chemical methods.

B. Biochemical Preparations Program.

Dr. George Overend, Research Associate: selection and preparation of crystalline biochemical derivatives; advisor on significance of biochemical problems.
Gina Overend, Research Assistant: preparation and chemical analyses of crystalline derivatives.
Maartje Eriks: preparation and chemical analyses of crystalline derivatives. (See also III B.)

Perhaps the most critical step in X-ray analyses of complex biochemical materials is the choice of compounds and the preparation of crystalline derivatives highly amenable to X-ray attack. Investigations in this phase of the biochemical research are supported by a grant from the Rockefeller Foundation; and the selection and preparation program has profited very greatly from the competence of Dr. George Overend and the enthusiastic assistance of Mrs. Overend. Mrs. Eriks has just been added to this program (April 26, 1952).

Advice on compounds for X-ray analysis, and crystalline material, has also been furnished by prominent biochemists from this country and abroad.

V. X-Ray Instrumentation Programs.

A. High-Brilliance Micro-Beam X-ray Techniques, for Diffraction Studies of Single Crystals of Microscopic Size.

Dr. R. Pepinsky, Research Professor: general instrumentation. (See also I A, II, III, IV.)
Kaj Drenck, Visiting Asst. Professor: micro-beam X-ray tube design; photon-counter goniometers. (See also III A, D.)
P. Frank Eiland, Research Fellow: microcrystal techniques; direct photon-counter goniometers. (See also I B, IV.)
Dr. Wiepko G. Perdok, Research Associate: micro-crystal techniques. (See also III A, IV.)
Teruo Noguchi, Research Assistant: scintillation-crystal photon counters. (See also I A, III D.)
Henri Diamant*, Research Associate: electronic and mechanical design.
Niels Olesen*, Research Assistant: mechanical design and construction.
Kenneth Ott, Technician: mechanician.

This program is concerned with the further development and the utilization of fine-focus high-brilliance micro-beam X-ray tubes, for diffraction studies of single crystals of microscopic size. Contractual support for the research is now being sought. As soon as funds permit, graduate students and additional technicians will be added to the group.

*Beginning June or July, 1952.

B. General X-Ray Instrumentation.

All investigators and technicians of V A, above, and in addition:

Ralph Myers, Technician: electronic circuit construction.
Samuel Meyers, Technician: electronic circuit construction.
James McCann, Technician: X-ray equipment maintenance. (See also III A.)
Melvin Johnson, Technician: X-ray equipment construction and maintenance.
Max Williams, Technician: general construction and maintenance.

This group is concerned with new construction and maintenance of general X-ray diffraction equipment and related instrumentation, including intensity-stabilizing and -measuring circuitry.

VI. Graphics Group.

Robert Ebeling, Chief Photographer.
Malcolm Eckley, Photographer. (See also I B.)
Silvia Silver }
Virginia Jeffrey } Photographic Assistants
Paul Wilmarth }
Thomas E. Quickel } Draftsmen.

VII. Office Staff.

Judith Needleman, Secretary.
Bertha Creasing }
Marion Gross }
Myrtle Karsten }
Sally Scullin } Stenographers.
Carmen Scott }
Sylvia Silver }
Henrietta Snyder }
Elizabeth Davis, Budget and Records Clerk.
Karin Drenck, Editorial Assistant.

VIII. Proposed Program on Neutron Diffraction.

A research program on neutron diffraction of single crystals, with particular application to transition studies, is under arrangement in collaboration with Brookhaven National Laboratory. This will, in essence, supplement present X-ray studies. Some staff members for this program have already been chosen. It is hoped that the program can be initiated by July, 1952.

IX. Laboratory Layout.

The present layout of the X-ray and solid state laboratory is shown in figure 1. The latest facility to be added is the Collins Cryostat for production of liquid helium, which will be installed in the space indicated on May 19-23.

All X-ray equipment will eventually be moved from present locations to room 7, adjacent to the present laboratory. The proposed arrangement of this X-ray laboratory is shown in figure 2. Space now occupied by the X-ray equipment will be utilized for desks and expanded solid-state facilities. The proposed ultimate arrangement of the present main X-ray room, which will be altered to provide office space, is shown in figure 3.

X. New Laboratory Personnel since May. 1952.

James Deysher	Draftsmen
Eugene Tomer	
Jean Martin	Secretaries
Norma Waters	
Richard Denton	Electronic Technicians
Michael Bubel	
Robert Petrosky	
Anthony Petrilla	
Charles Helenius	Laboratory Assistant
Elliott Burrell	Physical Chemist
William Pavelich	Inorganic Chemist
Tara Purshottam	Biochemist

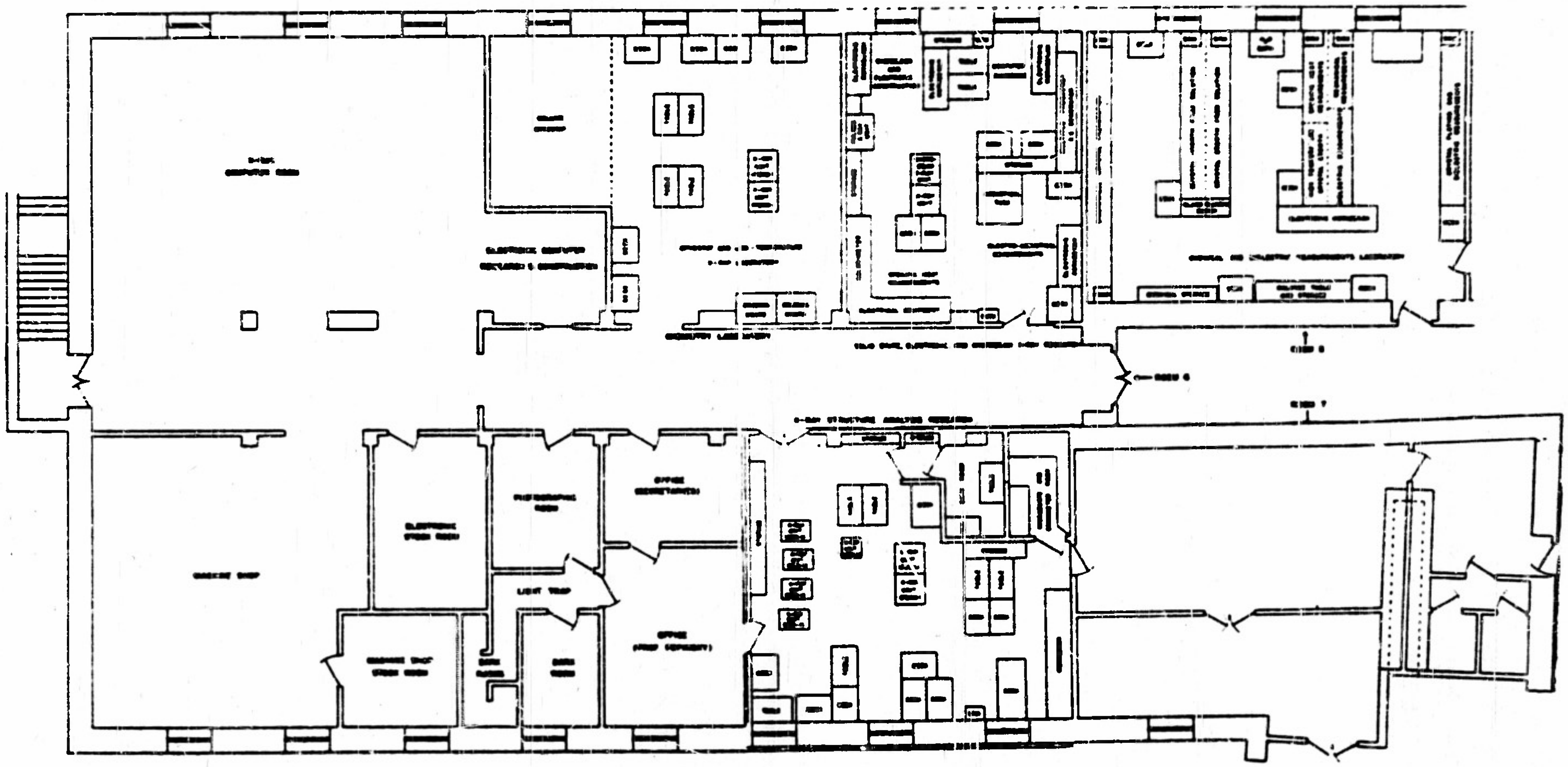


Figure 1.

Present Layout of X-Ray and Solid State Laboratories,
Department of Physics, The Pennsylvania State College.

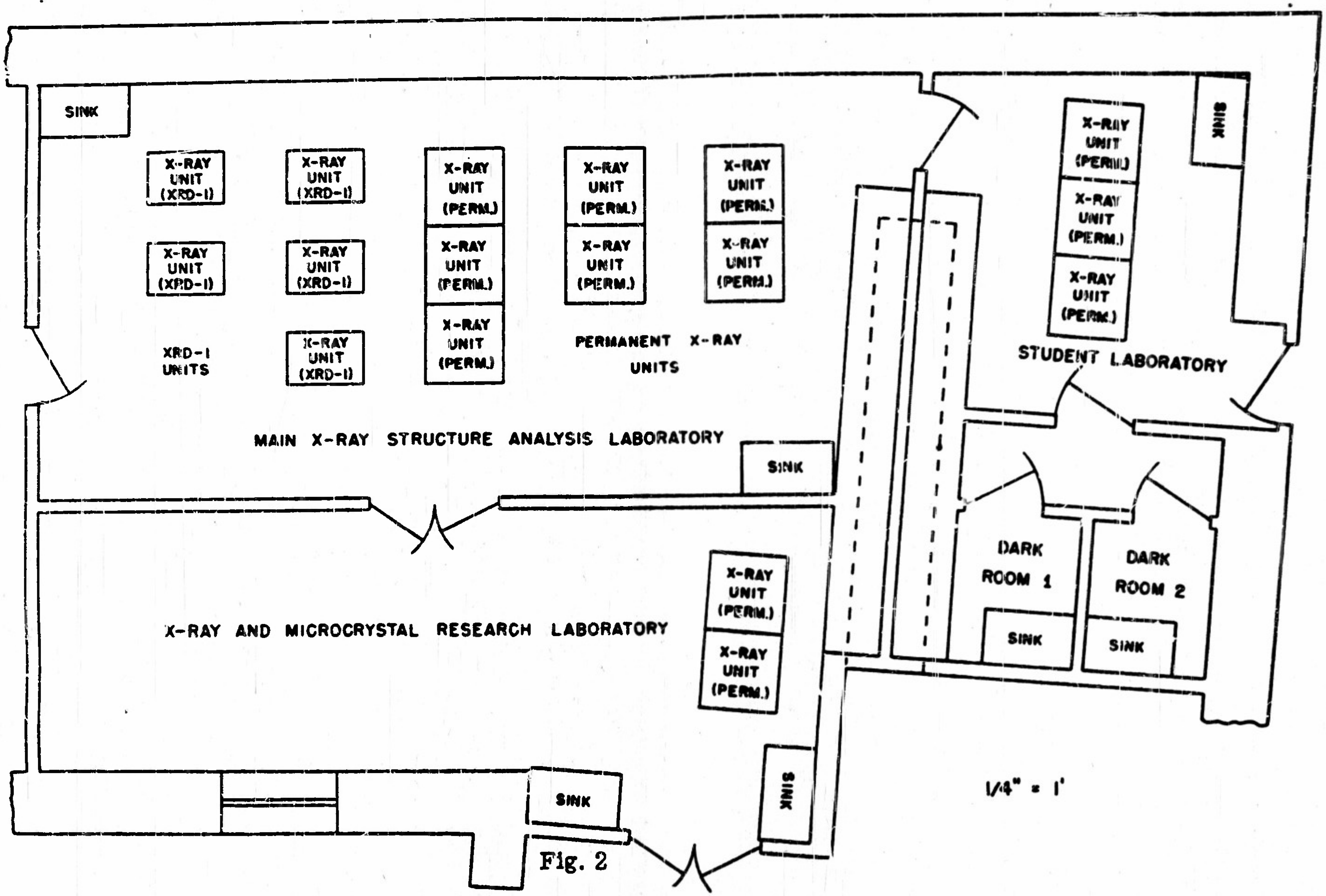
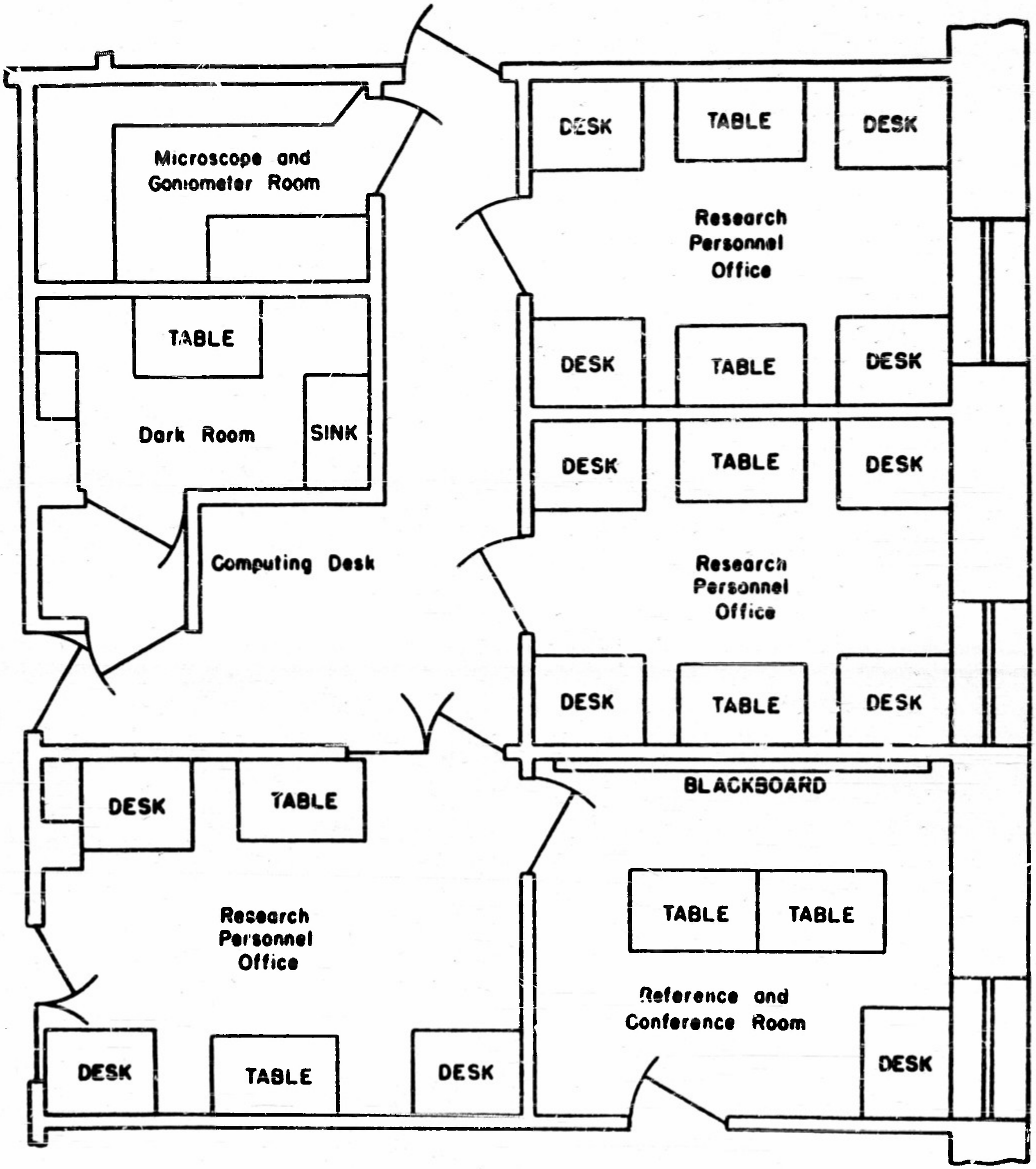


Fig. 2

Proposed Layout of X-Ray Units
Room 7, Osmond Laboratory



1/4" = 1'

Figure 3.
Proposed Arrangement of Present X-Ray Room, into Research Personnel Office and Conference Space.

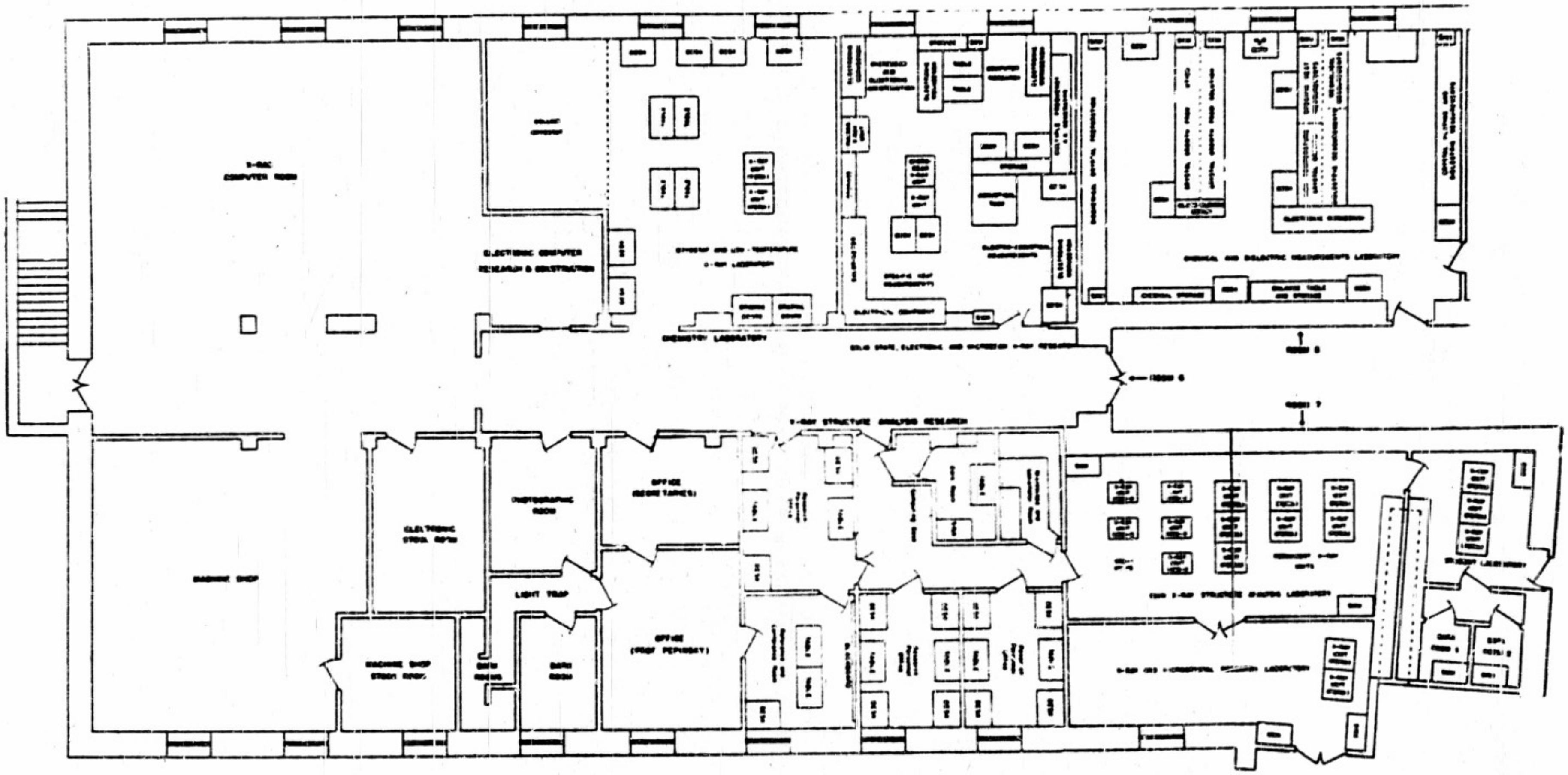


Figure 4.

Ultimate Layout of X-Ray and Solid State Laboratories, Department of Physics, The Pennsylvania State College.

Biochemistry Research

W. G. and G. O. Overend.

To date the work of the biochemists of this Department may be divided roughly into three aspects. Firstly, a survey is undertaken of compounds of unknown structure, which have important biological properties. Often compounds are provided by the original investigators, who inquire whether information regarding structure can be furnished by X-ray methods. A thorough literature research is undertaken and the results are condensed into a brief but critical review of knowledge about the compounds and of the problems requiring solution. An appraisal is forwarded of the value of X-ray methods in solving the problems posed, compared with the possibility of their solution in a commensurate time, by the methods of classical organic chemistry.

After the decision is made to undertake an X-ray structural investigation of a particular compound, suitable derivatives such as salts, isomorphous pairs or complexes containing heavy atoms are prepared. This often involves the development of a variety of crystallisation techniques. Close liason is maintained with the X-ray analyst to insure that, as far as is practically possible, he is provided with crystalline derivatives of optimum size and habit and of favorable space group, thereby offering a maximum chance of success in establishing the structure of the compound. So far our main interests have been concentrated on certain alkaloids, such as jervine, gelsemine, etc., some antibiotics, for example terramycin and aureomycin, and certain carbohydrates like heparin and the Schardinger Dextrins. However, many other compounds of biological interest have been appraised and the information about them recorded for future use. Among such compounds are desoxyribonucleotides, fumagellin, α-lipoic acid, visnagen, nocardamin, citrovorum factor, coumingine, macrozamin, dianhydrohexitols and cordycepin.

Finally considerable time has been expended in equipping this small biochemical unit, to make it an efficient adjunct to an X-ray crystallography laboratory which has particular interest in crystalline biochemicals of physiological or medicinal value.

X-Ray Investigation on the Structure of Aureomycin and its Related Compounds

T. Watanabe and T. H. Doyne

We have established the isomorphism between aureomycin and terramycin hydrochlorides. This suggests that the molecular structures of these two antibiotics is closely related. We have also found another modification of terramycin hydrochloride. At present we are studying the crystal structure of aureomycin hydrobromide, the crystals of which were first prepared in this laboratory. The unit cell dimensions and the space group of aureomycin hydrobromide are:

$a = 28.24$, $b = 20.79$, $c = 8.35$, $z = 8$, C222.

The two-fold symmetry axes running to the three principal axes permit us to make use of the criterion that there should be no appreciable electronic density along these axes, as well as the usual non-negativity criterion.

X-Ray Analysis of Podophyllotoxin

Bromo- and Chloro- Acetates

W. G. Perdok

Since the X-ray analysis of bromo-podophyllotoxin, as previously reported from this laboratory in the review of Sept. 1, 1951, gave no straightforward solution to the problem of the molecular structure of this important mitotic poison, a new attack on this problem, via the halogen acetic esters of the compound, appeared necessary.

Podophyllotoxin is the most important compound found among a number of drugs that can be extracted from the root of podophyllum peltatum (May-Apple). It is of physiological interest for reason of its antimitotic activity. On injection it causes severe damage to malignant tumours in mice, in a rather specific way, so that a knowledge of its structure is of importance in the chemotherapeutical attack of the cancer problem. Though much is already known about the molecule of podophyllotoxin from chemical investigations, the structural formula is not yet established, particularly as to the stereochemical configuration of the lactone ring. No method is more straightforward for the solution of stereochemical questions than X-ray analysis of crystalline compounds, provided that a compound can be found which allows a direct solution of the structure analysis by the heavy atom or isomorphous substitution method. Up to now the first approach was applied to bromopodophyllotoxin, but this did not give enough information to indicate a definite stereochemical structure for the podophyllotoxin molecule. Therefore a new attack has been made on this problem following the second method of isomorphous substitution using the halogen acetic esters of the compound. These esters, recommended by and available from Drs. J. Hartwell and A. W. Schrecker of the National Institute of Health, might be expected to exist in isomorphous crystals. The esters were prepared and kindly put at our disposal by Dr. Schrecker.

The melting points, as measured by Dr. Schrecker, are:

Compound	M.P. (immersed at 150°C)	M.P. (immersed at 190°C)
podophyllotoxin-chloroacetate	208°-209°	209°-210°
podophyllotoxin-bromoacetate	190°	195°
podophyllotoxin-iodoacetate	192°	196°

The melting is accompanied by decomposition, and the samples immersed at the higher temperature gave higher melting points for this reason.

The morphological and optical investigation of these compounds indicated strongly that the crystals were orthorhombic and isomorphous. The crystals are prismatic needles, terminated by two small faces. These latter faces gave weak but sharp reflections on the two-circle optical goniometer, while the prism faces gave unsharp or multiple signal images. Consequently the axial ratios a:b and c:b were less accurately determined than that of c:a, from the morphological observations.

Morphological data:

orthorhombic: a:b:c = 1.15 : 1 : 0.58,

c:a = 0.506.

Observed forms: a (100); m (110); r (101).

angles:	φ	ρ
b (010) not obs.	0°	90°
m (110)	41°	90°
r (101)	90°	26°51'

A drawing of the crystal is shown as figure 1.

The crystals are quite strongly double-refracting; they extinguish parallel to the prism edge (c-axis), the c-axis being the direction of the "slow" vibration in comparison to the b-axis. The optical axial figure through (100) was typical of a two-axial

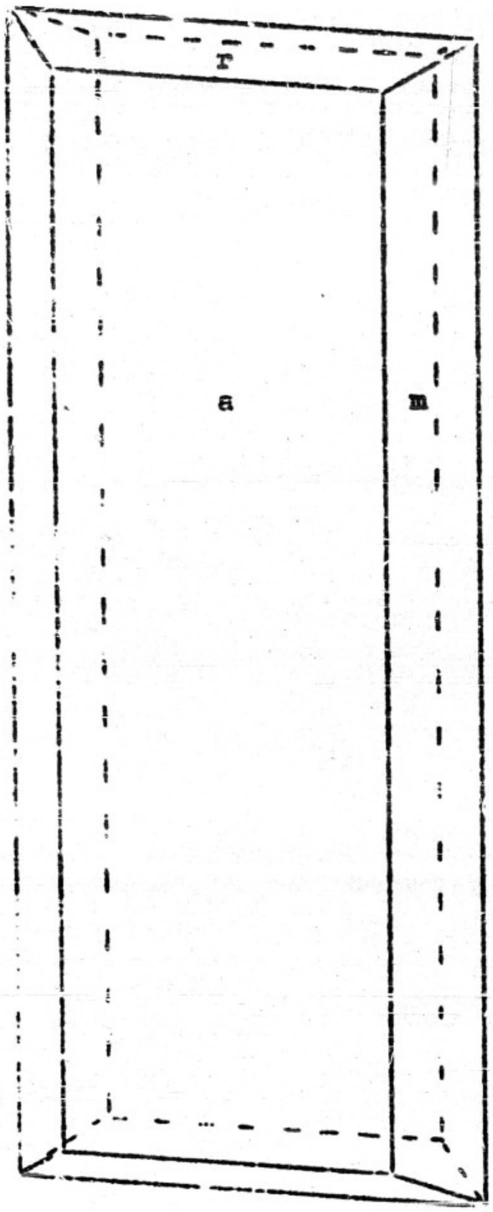


Fig. 1.

Morphology of

Podophyllotoxin Bromo-acetate

crystal perpendicular to the obtuse bisectrix. To check the morphological development against the X-ray unit cell, oscillation photographs were taken of the bromo-compound about the three crystallographic axes. All those photographs showed a symmetry line perpendicular to the rotation axis; thus the crystal belongs definitely to the orthorhombic system, a higher symmetry being excluded by the optical properties. From the oscillation photographs the cell dimensions were calculated as a = 17.5Å, b = 15.3Å, and c = 8.7Å, giving the axial ratios a : b : c = 1.15 : 1 : 0.57, agreeing with the morphological axial ratios within the limit of errors.

The volume of the unit cell is 2340Å^3. The molecular weight of podophyllotoxin-bromoacetate, $C_{24}H_{23}O_9Br$, is 535.34, and the density of the crystal is calculated as 1.528 for 4 molecules in the cell. An experimental density determination gave the value 1.51.

For the chlorine compound, $C_{24}H_{23}O_9Cl$ (M.W. = 490.88), the calculated density is 1.39; the experimental determination also gave the value 1.39. These determinations were made in Thoulet's solution because of the high solubility of the compounds in organic heavy liquids like chloroform, bromoform, etc.

Determination of space group.

Weissenberg photographs of the zero, first and second levels were taken with the crystal rotating about the c and b axes.

The c-axis photographs showed two axes at an angle of exactly 90°. Moreover, both axes were symmetry lines of the Weissenberg pattern. The spacing on the axes were 17.6 and 15.3Å respectively, in agreement with the spacings found on the oscillation photographs. The only zero level photograph showed extinction restricted to the axes, h00 and 0k0 being observed only when h and k are even.

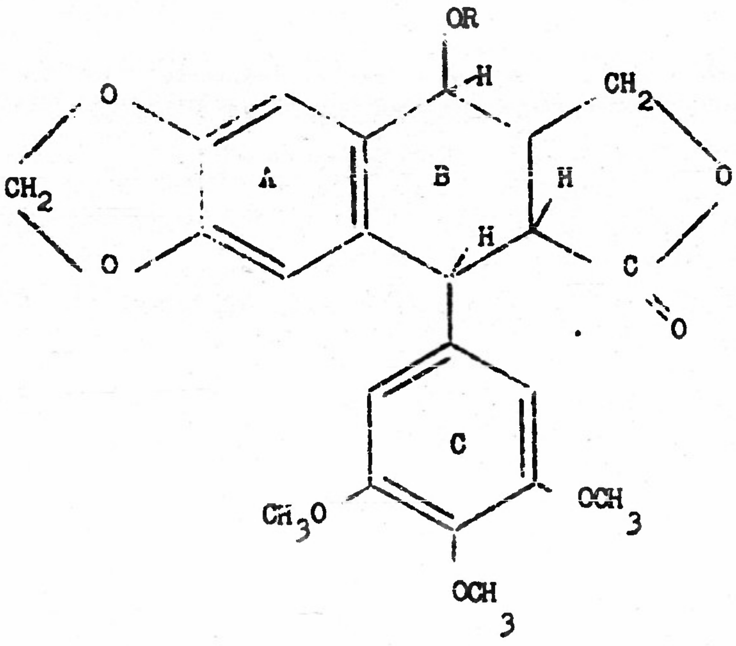
The b axis photograph again showed two axes at an angle of 90°, both being symmetry lines of the pattern. The spacings on the axes now were found to be 8.7Å and 17.6Å, in agreement with the values found before. Again the only extinctions were h00 and 00l when h or l are even. These extinctions indicate uniquely that the space group is $P_{2_12_12_1}$ (D_2^4). As this space group has only fourfold positions, the number of molecules in the unit cell must be 4 or a multiple of 4; and the density and cell constants had already indicated 4 as the multiplicity. There is no reason why the heavy atom should be in a special position, so there is a very good chance that a straightforward solution can be accomplished.

Preliminary considerations of the structure.

The b-axis of bromo-podophyllotoxin has a periodicity of 8.8Å. This invites comparison with the c-axial length, 8.7Å, in the haloacetates. The b-axis in bromo-podophyllotoxin was shown to be perpendicular to the more or less flat molecule; and it seems that the podophyllotoxin residue in the case of the haloacetates is essentially perpendicular to the c-axis. The similarity in this spacing suggests, furthermore, that the haloacetate chain extends in the plane of the molecule. In the bromoacetate the (001) reflection is very strong in the second order, missing in the fourth, and very weak in the sixth. This indicates a flat molecule with its plane perpendicular to c, and separated in the c-direction by 1/2 c. This separation, of 4.4Å, is a reasonable thickness for a nearly flat molecule.

Figure 2.

Proposed Structure of Podophyllotoxin Derivatives.



Hartwell and Schrecker's proposed structure for the podophyllotoxin derivatives is shown in Fig. 1, above.

$R = H$:	Podophyllotoxin;
$R = -O-\overset{O}{\overset{\|}{C}}-CH_2Cl$:	Podophyllotoxin chloroacetate;
$R = -O-\overset{O}{\overset{\|}{C}}-CH_2Br$:	Podophyllotoxin bromoacetate;
$R = -O-\overset{O}{\overset{\|}{C}}-CH_2I$:	Podophyllotoxin iodoacetate;
Br in place of R:	Bromopodophyllotoxin.

The evidence that the molecule is nearly flat suggests that the $-CH_2$ and $-C=O$ residues on ring "B" are in a trans relationship. This is in agreement with the conclusions of Hartwell and Schrecker, based on chemical evidence; but it is too early to rely on the X-ray support for this arrangement.

The Crystal Structure of Some Hydrohalides of Jervine.

R. Collin and C. Corona

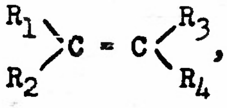
Jervine, with the empirical formula $C_{27}H_{39}O_3N$, is an alkaloid whose chemical structure has not yet been established. Jervine readily forms crystalline hydrohalides and four of these have been investigated. The unit cell and space group data for these crystals are as follows:

	a_o	b_o	c_o		Space Group
Jervine·HCl·CH_3OH	7.44 Å	10.0 Å	36.6 Å		$P2_12_12_1$
Jervine·HBr·CH_3OH	7.56	10.10	37.0		$P2_12_12_1$
Jervine·HI	11.00	7.92	16.28	112.6°	$P2_1$
Jervine·HBr	10.6	7.61	16.3	109.0°	$P2_1$

Phases for the ($h0\ell$) zone have been determined using both Jervine·HI and Jervine·HBr. These two compounds appear to offer the best possibility for a complete structure determination. The Fourier projections that have been obtained allow some deductions to be made as to the possible chemical configuration of the Jervine molecule.

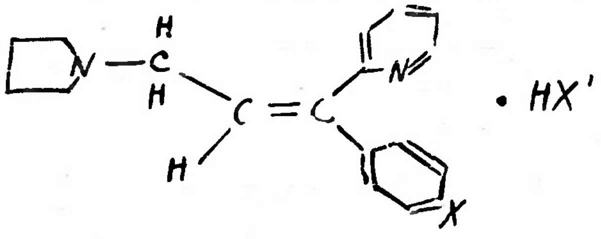
Crystal Structure of Some Antihistamines
1-(4-α- and β-halogenophenyl-1-(2-pyridyl)-3-pyrrolidinoprop-1-ene hydrohalogenides, $C_{18}H_{19}N_2X \cdot HX$

J. Rathlev

These compounds, which are of the type  $\begin{matrix}R_1\\R_2\end{matrix}\!>C=C<\!\begin{matrix}R_3\\R_4\end{matrix}$, show cis-trans isomerism. The so-called α-form is much the more potent antihistamine, but conclusive evidence for the relative positions of R_1, R_2, R_3 and R_4 in the two forms is not obtainable from chemical properties.

Since the α-form is triclinic, it presents a very difficult structural problem. The β-form proved to be simpler. It is monoclinic with the space group $P2_1/c$. Furthermore, two isomorphous derivatives of this form are available (a chloro- and a bromo-compound).

Fourier projections along the short a-axis (approximately 6 Å) showed the molecule clearly after several approximations. The configuration about the double bond is the following:



At present, the structure is in the process of refinement.

Crystal Structure of Castoramine

K. Eriks

The investigation of the structure of castoramine has just been started in this laboratory. Castoramine, isolated from beaver scent glands, is an alkaloid with the empirical formula $C_{15}H_{23}O_2N$. No chemical data about its ring-system are available, except that it is saturated, which suggests, that it is a pentacyclic compound.

The castoramine is obtained in the form of a sulfate and a selenate, which salts were found to be isomorphous, from optical and X-ray data.

The space group is orthorhombic, probably $P2_12_12$ or $P2_12_12_1$, with axes:

sulfate	selenate
$a = 15.2_7$	$a = 15.5_5$
$b = 12.8$	$b = 13.0$
$c = 8.7_2$	$c = 8.8_9$

The unit cell contains four molecules of the compound.

Bis-Cyclopentadiene Fe

$Fe(C_5H_5)_2$

F. Eiland

This crystal has been examined by X-ray methods and found to be in the monoclinic space group $P2_1/n$ with the lattice constants

$a = 5.94$

$b = 7.52$

$c = 9.00$

$\beta = 82°$.

A measured density of 1.516 gms/cc led to 2 molecules per cell. This places the Fe atoms in two related centers of symmetry and reveals that the molecules are centrosymmetrical. Intensity data using MoKα radiation is being collected and a structure analysis will be carried through via Patterson and electron density functions.

Antibiotic X.

F. Eiland

A structure analysis of the Rb salt of Antibiotic X ($RbC_9H_{14}NSO_3$) has been undertaken with no prior knowledge of the compound other than the emperical formula. From rotation and Weissenberg films the cell constants were found to be

a = 5.07

b = 8.35

c = 29.9

Sp.G. = $P2_1/n$

z = 4 molecules/cell.

The phases of the Rb and S atoms were used in the first Fourier synthesis. Subsequent Fourier syntheses were calculated by placing atoms at the positions of observed maxima. The second Fourier projection revealed a possible 5 atom ring containing the S atom. The structure was very recently solved by chemical means and use will be made of this development.

Single Crystal Geiger Spectrometer

F. Eiland

A single crystal Geiger spectrometer for accurate measurements of integrated intensity has been designed and constructed. The geometry of the target, pinhole and crystal is so arranged that a stationary crystal in proper position will have all planes of the same indices reflecting simultaneously. For this condition it is possible to monitor the target with a second Geiger tube and use a number of counts from it as a meter against which counts from the crystal can be compared. This by-passes the difficult problem of stabilizing the high voltage and tube current of the X-ray tube, for very accurate measurements of scattered intensities.

Image Seeking Machine

A. Moodie and T. Noguchi

Image seeking methods of Patterson function analysis recently introduced by Buerger have been shown to be powerful in crystal structure determination. Unfortunately they involve a considerable amount of labor when the functions involved are computed by hand. Further, as more powerful functions are employed the labor involved increases steeply.

It would therefore appear desirable to construct an image seeking machine, preferably employing the most sensitive function, the minimum function. In order to exploit the advantages of the image seeking method to the fullest extent the machine should, if possible, satisfy the following requirements:

(a) It should be capable of computing the minimum function continuously and displaying it as a two dimensional contour map.

(b) It should be capable of computing the function from a many-sided polygon.

(c) Variation of both the number and position of the vertices of the polygon should be readily achieved.

(d) It should be possible to employ bond angle and bond length data directly while image seeking.

The machine which is under construction appears to satisfy most of these requirements.

In essence the machine consists of a cylinder which can be rotated at 3400 RPM and translated at one inch per second. Two intensity modulated Patterson functions are fixed to the cylinder and stops adjusted so that after translation of one unit cell a reversal switch is made and the cycle repeated. The direction of rotation is not, of course, altered.

A polygon vertex is represented by a pickup head consisting of a fine lucite probe feeding a photomultiplier and cathode follower. The illumination for this probe is provided by a D.C. lamp, the light from which is focused by means of a lucite rod and lens.

The cathode follower, apart from providing a low impedance output, also forms half of the minimising circuit. This circuit consists of two diodes, suitably biased and connected across the cathodes of two cathode followers. Thus the minimum signal from any number of probes can be selected continuously.

The whole process, of course, contains non-linear elements. Nevertheless the non-linearity is the same for all probes so that a true minimum is selected.

The whole process is then linearised at the last stage by suitably choosing the levels at which a contour-line generator will fire. Time bases are driven from the rotation and translation so that, with a contour-line generator, an X-RAC type display can be achieved.

The direct use of bond angle and bond length data should be possible since the position of the probes will be controllable from a molecular model. The intensity modulated Patterson function can, of course, be obtained by a number of methods. Thus an X-RAC photograph without contour lines could be taken, or a purely optical synthesis could be employed.

Finally, however, a facsimile recording system is envisaged. Here, the X-RAC signal will be fed directly to a Phillip's lamp which gives light intensity variation up to 250 kc. The light from this lamp will be scanned across photographic paper synchronous with the X-RAC scans.

This method offers the considerable advantage of eliminating the spatial distortion inevitable on cathode ray oscilloscope displays, and the lesser advantages of decreased non-linearity in intensity, and rapidity.

Such a method of recording could, of course, be employed with the normal X-RAC contour line presentation.

Study of Perovskite Ferroelectrics

G. Shirane

(1) $(K\text{-}Na)NbO_3$: $KNbO_3$ is a ferroelectric which is of the same type as $BaTiO_3$, but the properties of $NaNbO_3$ are open to question. By the dielectric and structural studies of the phase diagram of $(K\text{-}Na)NbO_3$ we want to determine the essential differences in in the properties of $KNbO_3$ and $NaNbO_3$.

(2) $PbHfO_3$: Previous studies of $PbTiO_3$ and $PbZrO_3$ showed interesting dielectric properties in these crystals, so it is of interest to study $PbHfO_3$ in order to compare this crystal with the above two crystals.

Ferroelectric Compounds of the Ilmenite Type.

A. Magneli

The recent statement that lithium niobate and lithium tantalate show ferroelectric properties seems to be in conflict with the crystal structure data, which place these compounds among the non-polar structures of ilmenite type. This discrepancy has suggested further studies of this matter, including dielectric measurements (Dr. G. Shirane) and crystal structure studies, which have been started quite recently. In order to get further information concerning the crystal chemistry of niobium and tantalum, crystal structure investigations of the oxides of these elements (the high temperature modifications of the pentoxides) are now under way.

X-Ray Analysis and Dielectric Measurements of Transitions in the MH_2PO_4 Series

B. C. Frazer

All of the tetragonal crystals KH_2PO_4, KH_2AsO_4, RbH_2PO_4, RbH_2AsO_4, and CsH_2PO_4 have been reported to undergo ferroelectric transitions at low temperatures. We have recently found that CsH_2AsO_4 exhibits the same type of behavior. In addition, most of these have been studied and reported to be ferroelectric when deuterium is substituted for hydrogen. Crystals of $NH_4H_2PO_4$ and $NH_4H_2AsO_4$ also have low temperature transitions that appear to be related to the above, but neither of these becomes ferroelectric. Our interest in these compounds is from a structural viewpoint. We would like to find evidence in the changes in crystal structure, and through comparative crystal chemistry among the members of this class of compounds, for the mechanism of the transitions. In addition, we hope that the observed structural changes will provide an understanding of their anomalous dielectric behavior.

Considerable progress has been made recently in our study by the completion of an X-ray analysis of the transition in KH_2PO_4. The crystal has a relatively simple tetragonal structure above the transition point (122°K). It becomes orthorhombic below the transition, and with the absence of a center of symmetry in projection the structure becomes a somewhat more difficult problem. Although the room temperature structure is a well-known one, we redetermined it just above the transition point. The reason for this was two-fold. We wished to study the character of the relatively simple tetragonal case before proceeding to the more difficult orthorhombic structure. In addition we expected, and found, some small changes in the structure which could serve not only to provide a good starting point for the other structure but also might serve to throw some light on the mechanism of the transition. The two most significant findings of this preliminary analysis were the observation of a marked contraction in the hydrogen bonds (from 2.53 Å to 2.45 Å) and a change in KO_8 configuration. At room temperature each potassium is surrounded by eight practically equidistant oxygens. In the structure just above the transition point four of the oxygens are at one distance and the other four are at a definitely larger one. The larger distances are associated with nearest oxygens of PO_4 groups directly above and below the potassium (thinking of the tetragonal c-axis as vertical). Also observed, in the Fourier projections, was a strongly anisotropic temperature vibration of the potassiums parallel to the c-axis. In the structure below the transition, it was found that the potassiums were displaced by 0.08 Å along the c direction (relative to the phosphorus positions). The phosphorus atoms were found to have moved (relative to their practically unchanged O_4 tetrahedral surroundings) by 0.03 Å. These results are of particular interest in view of the ferroelectric polarization of the crystal parallel to the c-axis.

We have just begun crystal chemical study of the MH_2PO_4 series. There are two main points of interest here. The first is concerned with the depression of the dielectric constant and the raising of the Curie point when a larger alkali ion is used in the series. The second is the question of dimorphism exhibited by certain members of the series. In the cases of RbH_2PO_4 and CsH_2PO_4 and in certain of the deuterium-substituted compounds, monoclinic and tetragonal modifications exist.

The dielectric measurements have been conducted primarily to ascertain the Curie point in CsH_2AsO_4 and to compare dielectric constants in the series for the purpose mentioned above. Out of this, however, some very interesting measurements at elevated temperatures have been made. Among these has been the observation of dielectric hysteresis effects in CsH_2AsO_4 in its tetragonal phase. These are apparently not ferroelectric in origin, but they are of general interest and are being checked for possible ferroelectric nature. At present these studies are being conducted on other members of the series.

The Shattering Transition in $NH_4H_2PO_4$ and the New Low Temperature X-Ray Goniometer.

R. Keeling

I. The Shattering Transition in ADP.

- A. Relation of ADP to the ferroelectric dihydrogen phosphates KDP and RDP.
    1. Dielectric constant versus temperature curves for ADP compared to those for KDP and RDP.
    2. Mixed crystal studies show a linear decrease of ADP shattering transition temperature with increasing RDP content.
- B. X-Ray investigations to date.
    1. Room Temperature structure of ADP. Space Group $I\bar{4}2d$.
    2. Oscillation Photographs of low temperature modification, when indexed in terms of room temperature lattice yield reflections which are not compatible with room temperature structure.

II. New Low Temperature X-Ray Goniometer.

- A. Purpose: The study of low temperature ferroelectric and related transitions.
- B. Adaptable to oscillation, Weissenberg and powder photographs and to Geiger Counter Measurements.
- C. Description.
    1. Mount.

2. Dewar.
3. Camera Carriage and Cameras.
4. Geiger counter spectrometer table.
5. Vacuum system.
6. X-ray tube and housing.

Structure Determination of $LiNH_4C_4H_4O_6 \cdot H_2O$

R. Vernon

A determination of the room temperature structure of $LiNH_4C_4H_4O_6 \cdot H_2O$ and its isomorph $LiRbC_4H_4O_6 \cdot H_2O$ has been made. The chief interest is in the ammonium compound which, as suggested by the data of Scholz,(1) Jaffe,(2) and Mason(3) have recently found to be ferroelectric below about 98°K by Matthias and Hulm,(4) and Merz.(5)

Weissenberg photographs were taken of both crystals. The space group was found to be $P2_12_12$ with four molecules per unit cell. Cell constants are given in Table I.

Table I.

Cell Dimensions for NH_4 and Rb Isomorphs.

Dimensions in Angstroms	a	b	c
$LiNH_4C_4H_4O_6 \cdot H_2O$	7.86	14.60	6.47
$LiRbC_4H_4O_6 \cdot H_2O$	7.87	14.68	6.35

Patterson syntheses on X-RAC quickly gave the positions of the heavy rubidium atoms, at $x = 0$, $y = 0$, $z = -0.065$ and symmetry-related points. Their positions are such that they contribute to only half of the structure factors. The Fourier projections based on the structure factor phases of the Rb atom thus add false symmetry to the true electron density. Various techniques were tried, to determine the structure from these ambiguous Fourier projections. A model of a tartrate molecule actually proved most useful. Atomic coordinates are given in Table II.

Table II.

Atomic Positions

NH_4	(0, 0 -.065)	$C_{(6)}$	(.28, .370, .815)
$O_{(1)}$	(.102, .063, .41)	$C_{(1)}$	(.210, .120, .45)
$O_{(2)}$	(.36, .125, .38)	$C_{(2)}$	(.155, .197, .59)
$OH_{(3)}$	(.99, .185, .64)	$C_{(3)}$	(.27, .211, .77)
$OH_{(4)}$	(.255, .135, .915)	$C_{(4)}$	(.255, .302, .91)
$O_{(5)}$	(.20, .290, .08)	H_2O	(.18, .42, .35)

A comparison of these structures is made with that of Rochelle salt, which is also ferroelectric.

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(1) H. Scholz, Dissertation, Gottingen, 1940.

(2) H. Jaffe, Brush Development Co., Final Report to U. S. Signal Corps, Contract No. W-28-003, Sc. 1583.

(3) W. P. Mason, Piezoelectric Crystals, van Nostrand, New York, 1950, p. 233.

(4) B. T. Matthias and J. K. Hulm, Phys. Rev. 82, 108 (1951).

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The Structure of Ammonium Metaphosphate Hexahydrate.

Kaj Drenck

The ammonium metaphosphate was prepared according to a method described by G. Tamann. On inspection for ferroelectric effect it showed a hysteresis loop, the dielectric constant, however, being low.

The X-ray examination gave as a result the space group C2 and the lattice constants:

$$a = 20.1_6 \text{ Å}$$
$$b = 6.9_4 \text{ Å} \qquad \beta = 99.1^\circ$$
$$c = 6.4_5 \text{ Å}$$

The cell dimensions suggest that the compound may be a dimetaphosphate although such a compound has not previously been observed.

Specific Heat Measurements

H. R. Danner and E. J. Rock

A vacuum adiabatic calorimeter has been constructed to investigate the anomalous specific heat curves of ferroelectric crystals exhibiting transitions between 90° and 300°K. Measured amounts of heat are added electrically to the substance, the specific heat of which is to be determined, and the corresponding temperature rises are computed by extrapolating the observed equilibrium temperature drifts before and after each heating period. A series of such observations enables one to plot C_p versus lnT for a substance over an extended range of temperatures. The graphical integration of this curve between the temperatures T_1 and T_2 gives the entropy change between these temperatures. The postulation of a "normal" heat curve allows one to find the entropy change due to the transition alone.

The apparatus includes the calorimeter proper, consisting of the inner container, the adiabatic shield, and the vacuum jacket, and the associated electrical circuits for determining and controlling the temperature and measuring the energy added to the substance investigated.

Research on Ferroelectric Transducers

P. Tamarkin and W. J. Canty

The work on ferroelectric transducers, a phase of the general ferroelectric program being carried on in these laboratories, may be divided into two major parts. The first part, presently being developed, is to assess known and forthcoming ferroelectrics from the point of view of their ability to transduce electrical signals into acoustical ones. The second phase of the transducer program is, at the moment, a projected plan to explain in part the physical basis of the transducing ability of a particular ferroelectric from the viewpoint of electrical and acoustical energy losses.

Assessments of the relative merits of various ferroelectric transducers will be made by measuring directly the ratio of acoustical power output to electrical power input. The ferroelectrics will be formed into ceramic disks under varying conditions of temperature, pressure, binding agent, selected impurities, etc., and will serve in turn as the source of an acoustic beam propagated into water contained in a tank. This beam is obtained by applying, to the transducer, pulsed electrical carrier signals having a frequency range of 50 kc to 1mc. The resulting acoustical field will be scanned by a small pressure-measuring microphone made of barium titanate. The electrical output of this microphone is amplified and presented on an oscilloscope. (The pulse method is used to differentiate between the signal directly incident on the microphone and those reflected from the walls of the tank, which can thereby be limited in size.) From the pressure measurements, pointwise intensities can be calculated and integrated over the solid angle of the beam thus giving the acoustical power output of the transducer. Simultaneously measurements of the electrical power input are to be made and thus the electro-acoustic efficencies of the transducers can be calculated, and then used to indicate the most suitable ferroelectric and method of preparation.

The procedure described above will give an immediate indication of the transducing ability of a ferroelectric and is thus of practical importance. However, the explanation of this electro-acoustic behavior will be forthcoming only upon gaining a knowledge of the inherent sources of electrical and acoustical energy losses in the ceramic and single crystals, as well as of the piezo and elastic coefficients of the ferroelectric. As a second part of the transducer program we intend to determine these characteristics, confining ourselves initially, at least, to an extended study of the sources of energy losses. Experimental details of this study have not yet been planned however.

On The Theory of Ferroelectricity in $BaTiO_3$.

G. Barsch

Among all crystals with polar (non-centrosymmetric) structures those exibiting a permanent electric polarization are of particular interest concerning empirical knowledge of the forces acting in crystals. These electrically polar crystals can be classified into two groups: they are called pyroelectric if the spontaneous electric polarization cannot be influenced by an external electric field, and they are called ferroelectric, if the spontaneous polarization can be reversed by an electric counterfield. Most of the ferroelectric crystals known so far show transitions and follow a Curie-Weiss law for the dielectric constant. Any theory of electrically polar crystal has to account for the following empirical facts:

1. The occurrence of a polar structure of a given compound; the stability of a certain structure as a function of temperature and the occurrence of transitions.
2. The numerical value of the spontaneous polarization and the law of its temperature dependence.
3. The (numerically high) value of the dielectric constant and the law of its temperature dependence.
4. The numerical value of the coercive field of single crystals and polycrystalline material and the law of its temperature dependence.

In particular it must be shown that the coercive field for those crystals, which are known as pyroelectrics, is greater than the dielectric breakdown field strength.

While the task mentioned under point 1 has not as yet been solved absolutely, various attempts have been made to explain the facts of points 2 and 3. The most elaborate theories are those by Devonshire and Slater. However even these theories are, in general, more qualitative than quantitative in the description of the empirical phenomena. A quantitative theory has been attempted in this laboratory in extension of a theory by Born on the temperature dependence of the pyroelectric moment.

An Improved Apparatus for Rapid Qualitative Testing on the Piezoelectric Effect of Crystals

C. McCarty

Piezoelectric crystals play a very important part in modern oscillating circuits, and therefore new materials with strong piezoelectric coupling and low temperature coefficients are in demand. For this reason, and also to aid in determining the symmetry of crystals, it has become necessary to have a piezoelectric crystal detector that will give quick, reliable, qualitative results.

The apparatus being constructed is base on the Giebe-Sheibe principle and uses a frequency modulated signal to produce the frequency variations that are applied to the crystal. The circuits have been designed by Prof. Perdok, and his experience with related equipment is of very great value to us.

The frequency modulated signal can be adjusted to a band width of 50 kilocycles, which changes over this range at 60 cps. With this apparatus the piezoelectric effect of crystals may be observed on an oscilloscope or detected by earphones.

Growth of Inorganic Crystals

W. Scheyer and E. Zemyan

Crystals are grown in this laboratory from melts, solutions, and the vapor phase. Special techniques are utilized when highly insoluble materials must be prepared from solution, and a large amount of work has been done in gels.

For synthesis of crystals from melts there are available two globar furnaces, a Huppert commercial furnace, a platinum furnace, and a high induction furnace. Other furnaces have been constructed for special purposes. The rates of heating or cooling can be controlled as desired by means of Brown and Leeds and Northrup potentiometers and recording devices. The temperature ranges available are from -5°C to 2300oC.

Ingredients for synthesizing crystals from melts are usually the oxides and carbonates, with fluxes if necessary. Because of the high melting points of some of the reactants, ceramics are sometimes prepared.

Where possible, crystals are prepared from their water solutions. In the case of simple salts it is preferred to prepare the water solution from the reaction of the acid and base rather than by double decomposition. However, if the addition of one solution to another leads directly to a precipitate, special devices such as diffusion tubes can be used. Gels, which are used as slow diffusion and minimum nucleation media, often yield crystals which cannot be prepared directly from their solutions. Constant temperature baths (both a cold water bath and oil baths) can be regulated for any temperature within the range -5° to 100°C.

Identification of crystals can easily and quickly be made by goniometric or microscopic means, or by X-ray studies. If any doubt exists as to the stoichiometric composition of the crystals, chemical quantitative analysis is used.

Dielectric Measurements Program

J. McLaughlin, M. Eriks

and E. Francis.

An apparatus has been constructed to measure the dielectric properties of crystals over a temperature range from -193°C to 700°C. Temperatures from room temperature to -193°C are obtained by surrounding the crystal holder with liquid nitrogen. For temperatures above room temperature up to 700°C, a furnace is used. It is also possible to check the crystal at any time for hysteresis loops.

The present series of experiments are for the purpose of studying solid solutions of $KNbO_3$ and $NaNbO_3$. The prime purpose of this program is to investigate crystals of varied chemical composition for structural phase changes and ferroelectricity. Since no accurate method of predicting a ferroelectric structure has been found, these investigations are to screen all crystals which can be grown.

New crystal holders are to be designed for the simultaneous measurement of a standard substance and an unknown substance. It is also now possible to use liquid helium to obtain temperatures down to -269°C.