Conf-780822--1

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LA-UR -78-1952

TITLE: X-RAY DIFFRACTION ON RADIOACTIVE MATERIALS

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SUBMITTED TO: 27th Annual Conf. on Applications of X-Ray Analysis, August 1-4, 1978, Denver, CO

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ENERGY RESEARCH AND
DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

X-RAY DIFFRACTION ON RADIOACTIVE MATERIALS*

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ABSTRACT

X-ray diffraction studies on radioactive materials are discussed with the aim of providing a guide to new researchers in the field. Considerable emphasis is placed on the safe handling and loading of not-too-exotic samples. Special considerations such as the problems of film blackening by the gamma rays and changes induced by the self-irradiation of the sample are covered. Some modifications of common diffraction techniques are presented. Finally, diffraction studies on radioactive samples under extreme conditions are discussed, with primary emphasis on high-pressure studies involving diamond-anvil cells.

INTRODUCTION

X-ray diffraction studies have played and continue to play an important role in increasing our knowledge of materials containing radioactive elements. Diffraction techniques have been used to investigate hundreds of such materials thereby revealing, among other things, the complex chemical crystallography of the actinide elements and their compounds and alloys. This is an area of considerable practical importance and of basic interest as well. The crystal structures and mechanical properties of these materials change with the addition of even trace amounts of other elements. Another problem of practical interest, which is peculiar to radioactive substances, is the damage sustained due to irradiation, especially

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*Work performed under the auspices of the Department of Energy.

self-irradiation. Some materials are more resistant than others, and the processes involved are not yet completely understood.

This work is intended to provide a guide to researchers planning to study radioactive materials by x-ray diffraction techniques, and to give a brief review of the field. Only the more severe radioactive materials are treated here; thus the mildly radioactive substances, such as natural uranium and thorium and their compounds, are omitted. Discussed are the problems of safety, modifications of various x-ray diffraction techniques, and some of the special crystallographic properties and problems associated with radioactive materials. Examples are chosen chiefly from work done at the Los Alamos Scientific Laboratory or from work done by associates of the authors at other institutions.

SPECIAL CONSIDERATIONS

Safety

The first problem that should be discussed in the handling of radioactive materials is safety. Exposure to radioactive materials, even in the small quantities required for many types of x-ray experiments, is well-known to be dangerous. This point is forcefully brought home when one sees the reaction of a detector to minute amounts of the heavier transuranic elements. The procedures for dealing with this problem differ according to the type of radiation emitted and the chemical properties of the sample.

Procedures have been developed at Los Alamos for handling radioactive substances, particularly the actinides, in a routine way. Primary emphasis is of course on the prevention of accidents; but equally important is advanced planning of what steps are to be taken when something does go wrong. The procedures described below have been used for over thirty years without serious incident.

Almost all radioactive materials oxidize readily in air, and the oxide spalls off as very fine particles that can become airbourne and be inhaled. Materials such as plutonium, which are primarily alpha emitters, are not particularly dangerous unless incorporated in the body. Thus, the first requirement is that the radioactive materials should be handled in an inert-atmosphere glove box 1) to minimize oxidation and 2) to prevent airborne distribution of the finely-divided powder of the oxidation products.

For alpha emitters, it is sufficient to produce sealed samples in an argon-filled glovebox. There is no practical limitation on the time allowed to complete the sample preparation. Loading the sample in a glove box is not nearly as bad a handicap as it might seem. To illustrate these procedures, we given as an example the insertion of plutonium alloy powder into fine fused-quartz (not glass, which is more fragile) capillaries for Debye-Scherrer cameras.

After the plutonium alloy sample is in the argon-filled glove box, the oxide is first carefully filed or brushed off. This is not done for safety considerations, but rather to prevent the appearance of the oxide pattern on the film along with that of the sample. The bare metal is then filed with a separate file so that the filings drop into a glass dish. The filings may then be crushed or ground in a diamond mortar until the particles are fine enough to drop freely down the entire length of the capillary tube.

The capillaries themselves are drawn from 1/8" (inner diameter) fused-quartz tubing, and the 1/8" mouth serves as an adequate funnel for introducing the sample. The capillary is safely held for sample-loading manipulations in a one-hole rubber stopper which is fitted in a large test tube. The test tube has a hole in the side to equalize the inside and outside pressures during the cycling of the glove box airlock.

Once the samples are loaded into the capillary, a fused quartz fiber is dropped down the capillary to hold the sample powder in place. This fiber also keeps the sample from being sucked out during the evacuation of the airlock as the sample is removed from the glove box. The capillary is evacuated and sealed off in a fume hood adjacent to the glove box. The capillary is then loaded into a Debye-Scherrer camera in the open laboratory. The capillaries can almost always be mounted safely with no difficulties; however, precautions must be taken to confine any contamination that might result from accidental breakage during mounting. A pad of cheesecloth with a paper tissue folded into it is placed on the working surface of the bench. The capillary is then inserted into the wax in the brass plug while both are held a small distance directly over the cheesecloth.

If the capillary should break during mounting on the plug it will simply drop onto the cheesecloth pad without shattering. Because the radioactive material is not badly scattered, the pad can be simply folded over the broken capillary and plug and placed in a container for dioactive disposal. The operator examines his hands, clothing and the working area for the presence of any contamination. The rooms in which the samples and films are loaded are monitored with continuous alpha air monitors having audible alarms. If the alarm sounds, operations are terminated and the personnel are evacuated from the laboratory. A health physics group then must decide what procedures are involved to bring the laboratory back to normal operating conditions.

If one is working with strong gamma or neutron emitters, such as americium-243 or curium-244, these same procedures may be followed, but the time allowed is drastically curtailed (sometimes down to a few minutes). The temptation to examine the sample by looking at it at close range should be strictly avoided. Dosimeters must be used to monitor the whole body exposure. It is important to remember that the eyes are much more sensitive to radiation than the body as a whole and that the hands are somewhat less sensitive.

Background Due to the High Gamma Activity of the Samples

The high gamma activity of some materials, particularly the heavier transuranic elements, may blacken films in power diffraction cameras so much as to make the patterns unreadable. A similar problem is encountered with the detectors on powder diffractometers. Although the single-channel analyzers in the counting electronics are supposed to discriminate against radiation outside a relatively narrow wavelength or energy range, the backgrounds are always considerably higher than one would expect from naive considerations.

Several things can be done to reduce the backgrounds. The samples can be made no larger than absolutely necessary, to minimize the number of gammas produced. It is occasionally possible to chose an isotope which produces fewer gammas than other isotopes available. For many of the transuranium elements, CuKα radiation with a nickel filter over the film provides good diffraction patterns. The high intensity of the CuKα lines reduces the exposure times, and the nickel foil absorbs much of the radiation produced by the specimen. Americium-243, for example, emits copious radiation (including x-ray fluorescence) in the energy range 12-24 KeV as well as radiation at higher energies. The nickel foil absorbs the "band" of lower energy radiation very effectively. Nickel foil can also be used of course to reduce the backgrounds in diffractometers by placing it over the counter window. Still more effective perhaps would be the use of an x-ray monochromator between the sample and a well-shielded counter.

Energy-dispersive x-ray powder diffraction methods are also starting to be explored, a possibility independently conceived by Peterson and co-workers (1), Benedict and co-workers (2) and the authors. In this techique (3), "white" x-radiation is incident upon the sample and the pattern is collected at a fixed diffraction angle with high resolution solid state detectors. The diffraction peaks appear at various energies and the pattern is stored in a multichannel analyzer with the energy calibrated against channel number. The gammas and x-ray fluorescence lines appear largely as sharp spikes at their characteristic energies. It might also be hoped that energy-dispersive methods would be well suited for short-lived isotopes because the entire diffraction pattern is collected simultaneously with high (> 95%) efficiency. Preliminary experiments on americium-243 have revealed some problems (4). There is a high continuous background over the entire energy range up to 50 KeV. In addition, the "band" of radiation between 12-24 KeV makes observation of diffraction peaks in that region nearly impossible, and the AmL_I absorption edge further eliminates the region between 24-30 KeV. The use of smaller samples and more intense "white" x-ray sources should overcome the problem of the high continuous background, and the diffraction angle can be chosen so that the diffraction peaks lie above 30 KeV. Ultimately, it would be desirable to use a synchrotron radiation source because it would up to 1000 times more intense than conventional x-ray tubes and because it would extend the energy range beyond 70 KeV as well. In that case, the continuum backgrounds would probably be neglible. Most likely, however, all these improvements will not yield substantially better patterns than can already be obtained with film methods. The energy-dispersive technique will probably be most advantageous in high-pressure studies involving diamond-anvil cells where the use of other x-ray techniques is severely restricted, as discussed later on below.

Changes Induced by the Radioactivity of the Material

There are several types of changes that occur as a result of the radioactivity of a sample. These include self-irradiation damage, changes in the sample chemistry due to radiation damage and due to the presence of "daughters" and their compounds, significant raising of the sample temperature, and finally in some cases half-lives so short that it is extremely difficult to prepare and study the sample in the short time available. For this last reason in fact, the structures of a number of elements have not yet been determined. Besides exotic actinides, the list includes radon, astatine and francium.

Self-irradiation produces a variety of changes in the crystal structures. A study of Roof (5-7) on 238(80%)PuO_2 over a three year period illustrates some of the complexity of self-irradiation damage. A sample disk of this material approximately one centimeter in diameter and 0.25 cm thick was sintered at 1625°C just prior to the experiment. Plutonium-238 is intensely radioactive and the sample remained considerably above room temperature throughout the experiment. (In fact the radioactive self-heating is so great that a sphere of $^{238}PuO_2$ about 4 cm in diameter remains red hot due to the alpha activity, a property that allows it to be used for a thermoelectric power source.) In these experiments the lattice was damaged by self-irradiation and partly repaired during the course of the experiments. The lattice constant increased by a small amount for about 60 weeks, then decreased to an equilibrium value close to the original value after another 140 weeks. From line-broadening analysis, the strain in the lattice also first increased and then decreased, but to a value not far below the maximum strain; the crystallite size remained unchanged. Apparently, the initial swelling of the lattice was produced by the formation of interstitial helium atoms. Eventually these combine by diffusion to form bubbles and escape through cracks and channels in the material, th[illegible]owing the lattice constants to contract back toward their [illegible] values. The self-heating aided in this process by promoti[illegible]sion, but otherwise annealing effects seemed minor.

The energy liberated by alpha decay vastly exceeds normal chemical bond energies and can break down chemical compounds of radioactive elements. Peterson (1) reports two factors which yielded success with einsteinium halides: 1) a sample size and geometry that maximizes escape of the alphas, and 2) provision for a continual resynthesis system to reverse the chemical effects of self-irradiation and maintain a steady-state concentration of the compound studied.

In fact, it is for the compounds of the intensely radioactive elements, such as radium, polonium or einsteinium, that the art of studying radioactive materials with x-ray diffraction has been developed to its fullest. The high specific alpha activity of these elements limits studies of their compounds to very small amounts of material. For example, 7 mg of polonium produces 32 curies and one watt of heat and converts to lead at the rate of 0.5% per day (8). A further complication is the fact that most of the highly radioactive elements are also highly reactive chemically.

Thus, the x-ray studies on radium, polonium, einsteinium and their compounds must be done on 10-50 microgram quantities in inert atmosphere or vacuum. Moreover, the purification on the radioactive material must be done immediately before use, and both the x-ray studies and identification of the compounds must be done in a short period of time. The common procedure used in these cases is to create the compound of interest from the freshly purified radioactive element directly in the x-ray capillary. A variety of methods have been described for preparing samples, each tailored to the chemical reactions involved and the vapor pressures of the elements and compounds of interest (1,8-15). Procedures have been developed for producing a compound, x-raying it, changing it to another compound, etc. (1).

When chemical synthesis is done on such a small scale, the problem of identification of the compounds produced is not trivial. Witteman and co-workers (8) successfully identified simple polonium compounds with presumably well-defined stoichiometry by comparing the lattice constants with those calculated from ionic radii. Substances may also be recognized from their characteristic powder patterns, and a critical compendium of the wealth of diffraction data on actinides is being prepared by Roof (16) to provide the basis of compound identification. However, it is very difficult to tell the oxides and nitrides of many transuranic elements from the metals themselves from only the lattice constants. For example, americium and curium and their respective oxides and nitrides all have the fcc structure with similar lattice constants (9), to wit:

Am	a = 5.004 ± 0.002 Å	Cm	a = 5.038 ± 0.002 Å
AmN	a = 5.002	CmN	a = 5.041
AmO	a = 5.045	CmO	a = 5.09

Peterson (1) describes a microscope-spectrophotometer to record the absorption and/or luminescence spectrum of the sample as it is being studied with x-rays.

MODIFICATIONS OF COMMON DIFFRACTION TECHNIQUES

Except for monitoring for possible contamination, the operation of Debye-Scherrer cameras containing radioactive materials is not significantly different than for normal materials once the capillaries have been loaded according to the procedures described above.

Radioactive powder samples may also be studied on diffractometers outside of ventilated enclosures. Commonly, a mounted and polished metallographic specimen is used as the sample, but it must be sealed for work done in the open laboratory. This is usually accomplished by wrapping the sample in a thin sheet of a material that contains the contamination, is transparent to x-rays and has an x-ray pattern that will not obscure the pattern of the sample. The large amount of heat generated by plutonium-238 and higher specific activity materials precludes the use of any plastics. Instead the sample is loaded into a metal sample holder (in a safety enclosure) and covered with a thin metal foil window sealed with sticky lead tape. The preparation and subsequent handling must be done very carefully to avoid tearing the foil. When the sealed sample holder has been found free of contamination it may then be placed on the diffractometer in the usual manner.

Many radioactive materials have been studied with single-crystal techniques. A large number of compounds and alloys of plutonium have been studied in this way, and such a study has even been done on $CfBr_3$ (1,17). As with powder samples, the main concern is to prepare the sample so that particles, particularly of the oxide, are not scattered about. It is usually not possible to grow single crystals of plutonium alloys. For this reason, large-grained samples are broken in a mortar in a radiation safety enclosure if the material is sufficiently hard and brittle. The particles are then placed in a small bowl and covered with mineral oil or dilute Duco cement-butyl acetate solution to prevent oxidation. One fragment is then selected and mounted on a standard goniometer head in the usual way while the operation is viewed through a microscope. The bead of Duco cement protects the sample from oxidation, sometimes for years. The radioactivity of the sample can usually be an advantage in this case, because the fragment can almost always be found if it is accidentally knocked off during the loading procedure. Once the sample is mounted on the goniometer head, the usual single-crystal diffractometer or film methods may be used. There is no significant film blackening for patterns of plutonium compounds because plutonium is primarily an alpha emitter and because single-crystal patterns require much less exposure time than do powder patterns.

RADIOACTIVE SAMPLES UNDER EXTREME CONDITIONS

A number of studies at high and low temperatures and at high pressure have been made on radioactive materials. High-temperature studies are complicated by the high chemical reactivity and volatility of some radioactive materials. When small samples are required, even trace amounts of impurities in a nominally inert atmosphere or reactions with the capillary itself can alter the sample drastically. This is particularly vexing when the sample is supposed to be the pure metal. The procedures used to solve these problems depend on the nature of the substance studied, and have been discussed by several authors (1,9-12). Low-temperature studies are more straightforward. The principal problem is in cooling the sample. In practice, this is usually not too difficult for most radioactive substances of interest. To be sure, a material with a sufficiently high specific alpha activity may be impossible to cool very much; but plutonium 239 alloys or americium-243 can be cooled to a few degrees Kelvin without great hardship.

Interest in high-pressure studies on radioactive materials is rapidly expanding, primarily due to recent developments in diamond-anvil cell techniques. Radioactive materials have already been studied to pressures over 190 kbar using diamond-anvil cells. To date only film cassettes have been used in these studies, but several laboratories are setting up energy-dispersive x-ray diffraction systems.

In normal high-pressure studies with diamond-anvil cells, the sample is either 1) placed between the diamonds with no gasket around it, or 2) placed in the hole of an Inconel gasket with a hydrostatic fluid. In the first case very fine x-ray collimators are used so that the x-rays do not see a great pressure distribution. Larger collimators may be used with gasketed samples. Variations of both of these techniques have been successfully applied to the study of radioactive materials.

Roof (16) has used the non-gasketed technique on plutonium up to 190 kbar. Plutonium foil 0.025 mm thick was put between two aluminum foils, each 0.018 mm thick. This sandwich was then placed between two pieces of scotch tape to form the sample coupon, which was then placed in a Bassett (18) diamond cell. The aluminum also provided an internal pressure standard. Exposure times of 300 to 500 hours were required because of the fine collimators employed, but exceptionally clear patterns were obtained. There was no signicant film blackening from the plutonium gamma rays.

Burns and Peterson (19) have studied californium up to 140 kbar with a Bassett cell with the gasketed diamond cell technique. The sample of californium metal 0.1 mm in diameter was loaded into a tiny aluminum foil cup which was placed in the hole in the Inconel gasket. The sample was then covered with a small disk of aluminum foil. The operation was performed under a microscope in an inert-atmosphere glove box that was nominally "cold" inside so that the outside of the high-pressure cell was not contaminated. When pressure was applied, the sample was encapsulated in a can of aluminum. This arrangement contained the alpha-emitting californium-249, prevented oxidation by excluding air and provided an internal pressure probe from the aluminum lattice constants. Normal x-ray exposures ran between 18 and 24 hours.

The full advantage of diamond-anvil cells has not yet been used in studies of radioactive materials. We are setting up experiments that will use the diamond-anvil cell design of Mao and Bell (20-21), who have recently achieved 1.72 megabars sustained static pressure. Pressues are measured with the ruby fluorescence technique, which is both rapid and precise (22-24). Energy-dispersive x-ray powder diffraction will be used to explore phase diagrams and determine compressions. Energy-dispersive methods are very well-suited for use with diamond cells because strength considerations limit the size of the holes in the tungsten carbide diamond mounts and the optimum energy-dispersive diffraction angles are smaller than the angular apertures of the holes. The energy-dispersive technique also allows extremely rapid exploration of phase diagrams (25). Within 20 minutes it is possible to see whether the crystal structure at a new pressure is the same or grossly different from that at a previous pressure setting. Thus it is the ideal tool for the first exploration of the huge area of phase space now available.

CONCLUSION

We have endeavored to provide a guide to researchers embarking on projects involving x-ray diffraction on radioactive materials. We have discussed in detail those matters which we feel we are able to make a useful contribution to and have tried to give adequate references for subjects already treated in depth by other authors. We have emphasized basic safety considerations and have discussed many of the problems peculiar to studies on radioactive substances. We have also pointed out a major developing area; namely, the recently expanded possibilities of studying these materials with diamond cells to pressures possibly in excess of one megabar. We hope that this paper gives useful information on techniques and also gives a feeling for what the state of the art is at the present time.

ACKNOWLEDGMENT

One of us (D.S.) would like to thank D. T. Cromer, L. Schwalbe, and J. L. Smith for helpful conversations.

REFERENCES

1. J. R. Peterson, "Chemical Identification and Phase Analysis of Transplutonium Elements and Compounds via X-Ray Powder Diffraction," in H. F. McMurdie, C. S. Barrett, J. B. Newkirk, C. O. Ruud, Editors, Advances in X-Ray Analysis, Vol. 20, 75-83 (1976).

2. U. Benedict, private communication.

3. M. Mantler and W. Parrish, "Energy Dispersive X-ray Diffractometry," in H. F. McMurdie, C. S. Barrett, J. B. Newkirk and C. O. Ruud, Editors, Advances in X-Ray Analysis, Vol. 20, 171-186 (1976).

4. D. Schiferl, L. Schwalbe, J. L. Smith, R. Hagen, unpublished.

5. R. B. Roof, Jr., "The Effects of Self-Irradiation on the Lattice of 238(80%)PuO_2," in K. F. J. Heinrich, C. S. Barrett, J. B. Newkirk and C. O. Rudd, Editors, Advances in X-ray Analysis, Vol. 15, 307-318, Plenum Press (1971).

6. R. B. Roof, Jr., "The Effects of Self-Irradiation on the Lattice of 238(80%)PuO_2. II," L. S. Birks, C. S. Barrett, J. B. Newkirk, C. O. Ruud, Editors, Advances in X-Ray Analysis, Vol. 16, 396-400, Plenum Press (1972).

7. R. B. Roof, Jr., "The Effects of Self-Irradiation on the Lattice of $^{238}(80\%)PuO_2$. III," in C. L. Grant, C. S. Barrett, J. B. Newkirk and C. O. Ruud, Editors, *Advances in X-Ray Analysis*, Vol. 17, 348-353, Plenum Press (1973).

8. W. G. Witteman, A. L. Giorgi and D. T. Vier, "The Preparation and Identification of Some Intermetallic Compounds of Polonium," J. Phys. Chem. 64, 434-440 (1960).

9. R. D. Baybarz, J. Bohet, K. Buijs, L. Colson, W. Müller, J. Reul, J. C. Spirlet, J. C. Toussaint, "Preparation and Structure Studies of Less-Common Actinide Metals," in W. Müller and R. Lindner, Editors, *Transplutonium Elements*, pp. 69-77, North-Holland Publishing Co. (1976).

10. D. B. McWhan, B. B. Cunningham and J. C. Wallmann, "Crystal Structure, Thermal Expansion and Melting Point of Americium Metal," J. Inorg. Nucl. Chem. 24, 1025-1038 (1962).

11. B. B. Cunningham and J. C. Wallmann, "Crystal Structure and Melting Point of Curium Metal," J. Inorg. Nucl. Chem. 26, 271-275 (1964).

12. M. Noé and J. R. Peterson, "Preparation and Study of Elemental Californium-249," in W. Müller and R. Lindner, Editors, *Transplutonium Elements*, pp. 69-77, North-Holland Publishing Co. (1976).

13. F. Weigel and A. Trinkl, "Zur Kristallchemie des Radiums, I. Die Halogenide des Radiums," Radiochimica Acta 9, 36-41 (1968).

14. F. Weigel and A. Trinkl, "Zur Kristallchemie des Radiums, II. Radiumsalz vom Type $RaXO_4$, X = S, Se, Cr, Mo, W," Radiochimica Acta 9, 140-144 (1968).

15. F. Weigel and A. Trinkl, "Zur Kristallchemie des Radiums, III. Darstellung, Kristallstruktur und Atomradius des Metallischen Radiums," Radiochimica Acta 10, 78-82 (1968).

16. R. B. Roof, Jr., unpublished.

17. J. H. Burns, J. R. Peterson and J. N. Stevenson, "Crystallographic Studies on Some Transuranic Trihalides: $^{239}PuCl_3$, $^{244}CmBr_3$, $^{249}BkBr_3$ and $^{249}CfBr_3$," J. Inorg. Nucl. Chem. 37, 743-749 (1975).

18. W. A. Bassett, T. Takahashi and P. W. Stook, "X-Ray Diffraction and Optical Observations on Crystalline Solids up to 300 kbar," Rev. Sci. Instrum. 38, 37-42 (1967).

19. J. H. Burns and J. R. Peterson, "Studies of Californium Metal at High Pressures by X-ray Diffraction," for publication in the Proceeding of the International Conference on Rare Earths and Actinides, University of Durham, Durham, England (4-6 July 1977).

20. H. K. Mao and P. M. Bell, "High-Pressure Physics: The 1-Megabar Mark on the Ruby R_1 Static Pressure Scale," Science 191, 851-85 (1976).

21. H. K. Mao and P. M. Bell, "High-Pressure Physics: Sustained Static Generation of 1.36 to 1.72 Megabars," Science 200, 1145-1147 (1978).

22. R. A. Forman, G. J. Piermarini, J. D. Barnett, S. Block, "Pressure Measurement Made by the Utilization of Ruby Sharp-Line Luminescence," Science 176, 284-285 (1972).

23. J. D. Barnett, S. Block and G. J. Piermarini, "An Optical Fluorescence System for Quantitative Pressure Measurement in a Diamond-Anvil Cell," Rev. Sci. Instrum. 44, 1-9 (1973).

24. G. J. Piermarini, S. Block, J. D. Barnett, R. A. Forman, "Calibration of the Pressure Dependence of the R_1 Ruby Fluorescence Line to 195 kbar," J. Appl. Phys. 46, 2774-2780 (1975).

25. W. B. Holzapfel, K. Syassen and D. Schiferl, unpublished.