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APPARATUS FOR MAKING *X*-RAY POWDER PHOTOGRAPHS AT CONTROLLED, ELEVATED TEMPERATURES

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ABSTRACT

An *x*-ray powder camera for the investigation of substances at controlled, elevated temperatures is described. The apparatus differs in two respects from cameras previously described. In the first place, the film holder is removable without in any way disturbing the specimen or its condition in the furnace. In this way, the condition of the specimen may be independently controlled as desired while an exposed film is removed from the camera, developed, and another film substituted. This makes the apparatus especially suitable for the investigation of phase diagrams, for the specimen is never quenched or otherwise heat treated, except as desired. The apparatus also differs as to the method of maintaining the temperature of the specimen above room temperature, in that it is insulated against radiation losses rather than against conduction losses. This permits the construction of a furnace of negligible heat capacity, and because of this characteristic, the temperature of the specimen may be very rapidly varied, another feature of importance in phase diagram study. The temperature of the furnace at the specimen is calibrated by the investigation of substances having polymorphic transformations. The apparatus has been successfully employed in investigations up to about 600° C., and is suited to higher temperatures. The heating unit has also been adapted to the Weissenberg camera, which has been successfully used on a number of investigations of structural characteristics of single crystals at elevated temperatures.

INTRODUCTION

A number of devices have been described for making *x*-ray powder photographs of materials held at elevated temperatures.[1–12] Most of these

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[1] Westgren, Arne, Roentgen spectrographic investigations of iron and steel: *Jour. Iron and Steel Inst.*, **103,** especially 306–309 (1921).

[2] Westgren, Arne, and Lindh, Axel E., Zum Kristallbau des Eisens und Stahls: *Zeits. phys. Chem.*, **98,** especially 192–194 (1921).

[3] Becker, Karl, Eine röntgenographische Methode zur Bestimmung des Wärmeausdehnungskoeffizienten bei hohen Temperaturen: *Zeits. Physik.*, **40,** 37–41 (1927).

[4] Westgren, Arne, and Phragmen, Gösta, Zum Kristallbau des Eisens und Stahls II: *Zeits. phys. Chem.*, **102,** especially 3–4 (1922).

[5] Cohn, Willi M., Über einem Röntgenofen zur Vornohme von röntgenographischen Untersuchungen bei hohen Temperaturen und über einige vorläufige Ergebnisse für Pentaerythrit und Quarz: *Zeits. Phys.*, **50,** 123–136 (1928).

are cumbersome and also inconvenient to use and are evidently intended to be used where the experimental part of the research requires making a single photograph. When phase diagram studies are to be made, it is either too tedious to make use of such instruments or else their characteristics actually prohibit their use.

As an outcome of experience gained in investigating the phase diagram of the system Cu_2S-CuS by making x-ray photographs of samples held at controlled, elevated temperatures,[13] we have designed an improved apparatus for this purpose, and it has now been successfully used over a period of about three years. This apparatus has the following important characteristics for phase diagram studies: The specimen is not in any way disturbed in its heat treatment when the film is removed for development. When a new film is returned, everything is in adjustment for the next photograph, to be taken, presumably, at a different temperature. A novel furnace design permits changing the temperature level of the specimen almost instantaneously. There are therefore no delays in waiting for the furnace to come to the desired temperature.

Description of the Apparatus

General Features. Figure 1 shows a general view of the assembled apparatus. It fits, by means of a dovetail slide, onto a bracket which also supports the x-ray tube, Fig. 2. This arrangement permits the camera assembly to be easily removed and returned to its position with respect to the x-ray tube. The sliding motion of the camera is limited by an adjustable stop which permits recovery of exact position. The camera is adjusted to the x-ray beam as follows:

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[6] Jay, A. H., A high temperature x-ray camera for quantitative measurements: *Zeits. Krist.*, (A) **86,** 106–111 (1933).

[7] Wilm, D., Hofmann, U., and Endell, K., Über die Bedeutung von Röntgeninterferenzuntersuchungen bei hohen Temperaturen für die keramische Forschung: *Sprechsaal für Keramik, Glas, Email, Fach- und Wirtschaftsblatt*, Nr. **38,** 1–8 (1934).

[8] Finbak, Chr., and Hassel O., Kristallchemie der Nitrate einwertiger Kationen, II: *Zeit. Chemie* (B) **37,** 75–80 (1937).

[9] Schossberger, F., Eine Präzisions-Pulverkamera für Aufnahmen bei hohen Temperaturen und ein Messgerät für Röntgendiagramme: *Zeits. Krist.*, (A) **98,** 259–265 (1937).

[10] Straumanis, M., and Ieviņš, A., Die Bestimmung von Ausdehnungskoeffizienten nach der Pulver- und der Drehkristal-Methode: *Zeits. anorg. allg. chem.*, **238,** especially 180–181 (1938).

[11] Straumanis, M., Die Gitterkonstanten und Ausdehnungskoeffizienten des Tellurs und Selens: *Zeits. Krist.*, (A) **102,** 432–454 (1940).

[12] Wilson, A. J. C., The thermal expansion of aluminium from 0° to 650° C.: *Proc. Roy. Soc. Lond.*, **53,** 235–244 (1941).

[13] Buerger, Newton W., The chalcocite problem: *Ec. Geol.*, **36,** 19–44 (1941).

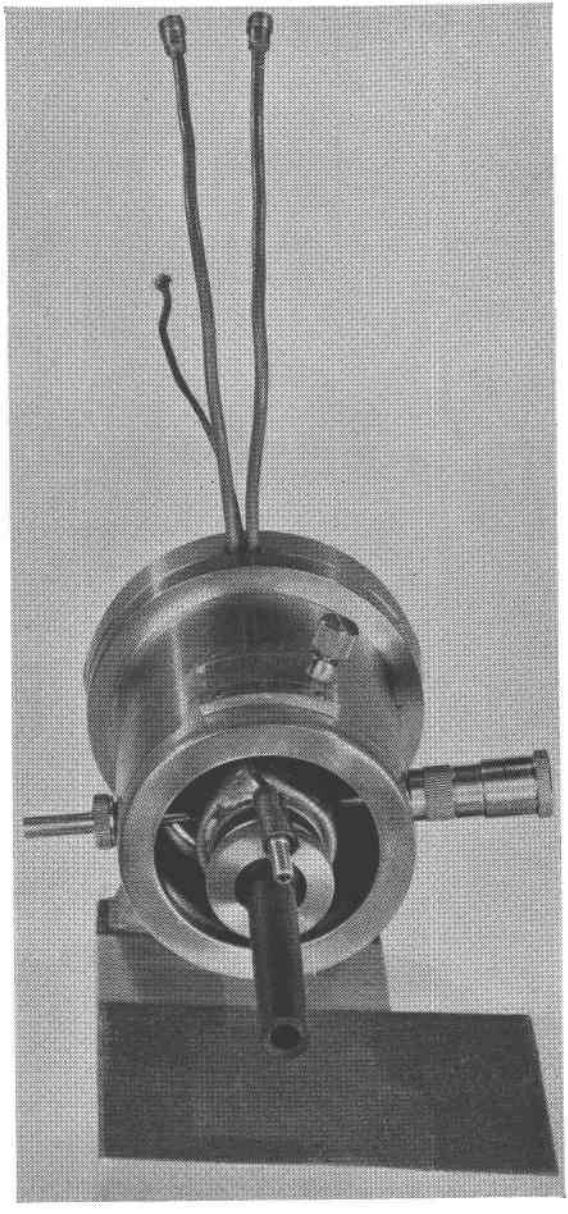


FIG. 1

(1) Vertical adjustment is achieved by sliding the bracket up and down on a keyed slide. Final position is fixed by tightening a screw.

(2) Horizontal adjustment is attained by sliding the cylindrical part of the camera in the direction of its cylinder axis and then clamping it to the sliding carriage by tightening the tangent screw, Fig. 6.

(3) Angular adjustment of the pinhole system to the slope of the x-ray beam is accomplished by rotating the cylindrical part of the camera in its clamp on the carriage, Fig. 6, and then tightening the tangent screw.

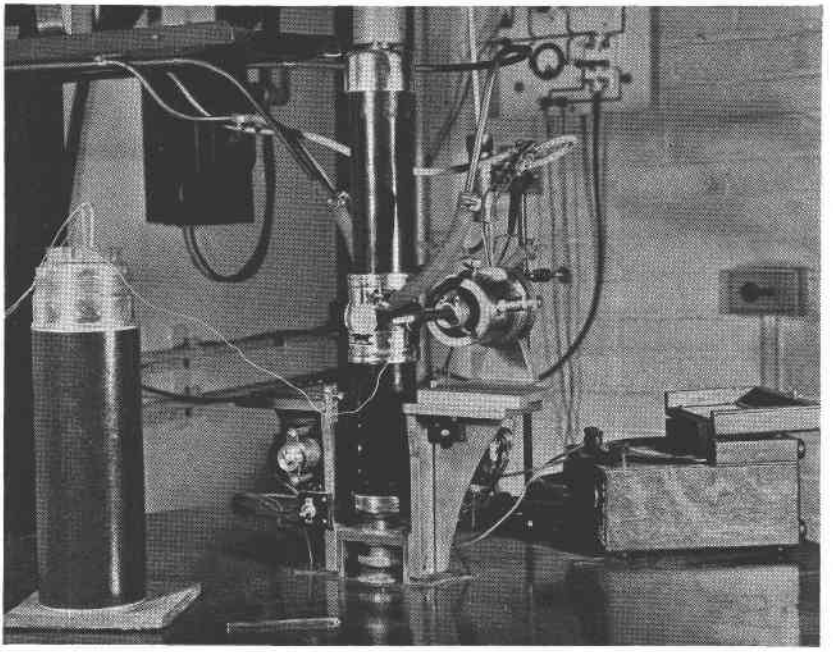


FIG. 2

These adjustments are not necessarily made in this order. It is possible to loosen both screws mentioned above, and adjust the whole bracket-camera assembly in the manner of a universal joint, until the x-ray beam is seen emerging in the exit port, as described beyond. Once the adjustments mentioned above have been made, the camera and its carriage may be removed at any time from the bracket and, on being returned, the apparatus exactly recovers correct adjustment with respect to the x-ray beam.

The bracket also carries a small Telechron motor which rotates the specimen. The motor is mounted on an insulating support and drives the specimen shaft through a rubber band belt. This precaution prevents

burnouts of the motor at times of temporarily erratic operation of the x-ray tube.

The general design described above is common to all powder cameras used in the Mineralogical Laboratory of the Massachusetts Institute of Technology, and in respect to these features and those of the camera proper (see beyond) they supersede the earlier design described by M. J. Buerger.[14]

Furnace Design. The furnace, which surrounds the specimen, is a removable unit, and is shown slipped off from its position at the left of Fig. 5*B*. In Fig. 5*C* it is shown in position.

The furnace unit is illustrated in detail in Fig. 4. It is believed that the system for maintaining temperature herein described is unique in furnace design. It is customary to maintain temperatures by surrounding the heating unit with insulation, i.e., by damming the heat flow by conduction barriers. In the tiny furnace here described, the temperature is maintained by damming the heat flow by radiation barriers. This is done by placing two very thin hollow aluminum cylinders about the heating unit. This device is nearly opaque to heat radiation but is transparent to the x-radiation diffracted by the specimen. This kind of heat barrier has the advantage over conduction insulation in that it occupies almost no space, since its functional barriers are surfaces, while the efficiency of conduction insulation depends upon its thickness, which causes it to occupy appreciable volume. Radiation barriers have the further advantage that they have negligible heat capacity, and so the temperature of the furnace can be very rapidly, almost instantaneously, changed to a new level at pleasure.

The actual furnace takes the form of a small capsule shown assembled in Fig. 3(*e*). This contains several concentric elements. The inner one is the heating element, a coil of #28 B. and S. gauge chromel "A" resistance wire. This coil is prepared by winding 9 turns symmetrically on each side of a $\frac{3}{16}$ inch diameter mandrel as shown in Fig. 3(*a*). This method of winding deliberately leaves a gap in the center of the coil through which the direct x-ray beam is to pass.

The heating coil is mounted by allowing it to expand within a porcelain tube (dimensions: 1 inch long and $\frac{3}{8}$ inch O. D.) whose chief function is to support the coil. To permit the diffracted beam to emerge from this tube, a transverse slot is cut in the porcelain, Fig. 3(*b*), covering all but about 70° of its circumference. This slot is widened somewhat at two diametrically opposite points to permit the direct x-ray beam to enter and leave without striking the porcelain.

[14] Buerger, M. J., An x-ray powder camera: *Am. Mineral.*, **21**, 11–17 (1936).

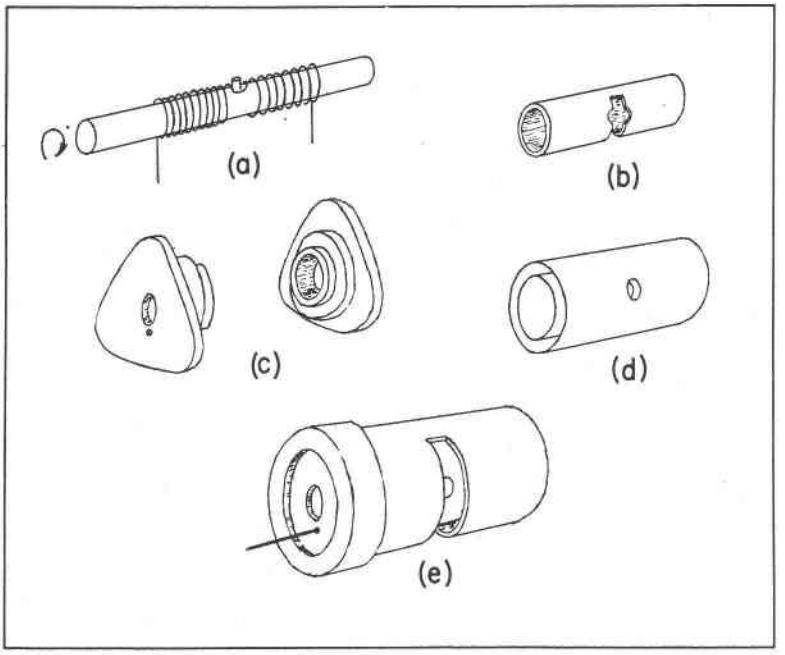


FIG. 3

The porcelain tube with its contained coil is thrust into two Transite spool ends, Fig. 3(*c*). These serve to axially centralize the tube in its protective copper cartridge, Fig. 3(*e*). The spool ends are not quite circular, but so shaped that they are supported within the cartridge on three circumferential points, thus minimizing conduction and consequent heat loss to the cooled copper.

The spool ends also support the aluminum foil radiation barriers. To this end they have two circular steps, Fig. 3(*c*); each supports a hollow cylinder of very thin aluminum foil (.0004 inch thick). Each aluminum cylinder is pierced with two diametrically opposite holes, Fig. 3(*d*), coinciding in position with the widened points of the slot in the porcelain cylinder. In assembling the furnace unit, all holes must be carefully lined up to permit the direct *x*-ray beam to enter and leave the cartridge. The technique of forming the aluminum cylinder is as follows. The sheet of foil, with entrance and exit holes carefully placed in computed positions, is laid on a flat piece of metal of its own width, and carefully shellacked on the edges where the foil is to stick to the spool and where it is to overlap itself. The spool is then rolled over the flat foil in the direction of its length, thus causing the foil to stick itself to the circular shelves on the spool ends and form the hollow cylinder.

The heating unit is placed within a copper cartridge, Fig. 3(*e*), for protection in handling. This has a slot coinciding with that of the porcelain cylinder in order to pass diffracted radiation from the heated specimen. As indicated in Figs. 4 and 3(*e*), the copper cartridge has an open back and front to minimize contact with the spool ends and thus reduce heat loss by conduction of transite to cold copper at this point. The skeleton cover has a screw fit.

One side of the heating coil winding is grounded to the cartridge. The other end protrudes from the front, insulated by the transite, Fig. 3(*e*).

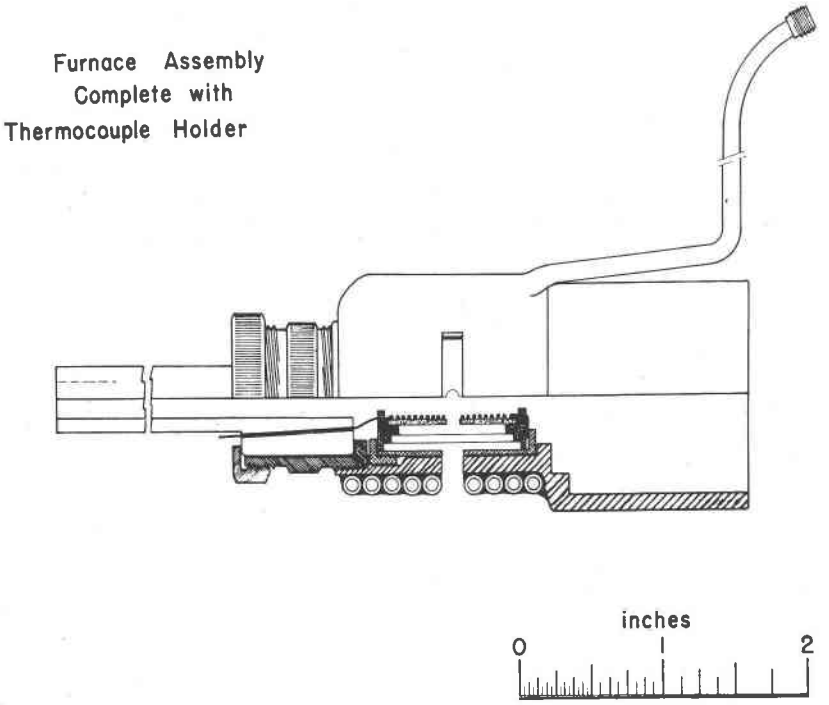


FIG. 4

The heating unit cartridge is held in place within a water-cooled jacket, Fig. 4, by means of a threaded metal member. The non-grounded lead to the heating coil is insulated from this by being led out through a fiber member, which also serves to hold a thermocouple, should this be desired (see beyond). The larger cylindrical jacket, Fig. 4, is wound with $\frac{1}{8}$ inch copper tubing for water cooling in the region of the cartridge, with the usual opening provided to pass diffracted radiation. The tubing is made an integral part of the jacket by being wiped with solder until all space

between coils and jacket is filled and the whole mass of metal becomes a unit. This cooling jacket has two functions:

(1) It protects the film against damage due to the high temperature of the furnace.

(2) It provides the apparatus with a definite ground-level of temperature. A definite amount of electrical energy is required to raise the apparatus by a definite temperature interval, ΔT, above this ground-level. Were it not for the cooling jacket, this ground-level would vary unpredictably with a number of external conditions.

The entire furnace jacket assembly, Fig. 5*B*, plugs into the camera spindle assembly as shown in Fig. 5*C*. From it projects three leads: (1) water entrance, (2) water exit, and (3) non-grounded lead from the heating coil. The grounded lead is the general metal parts of the apparatus.

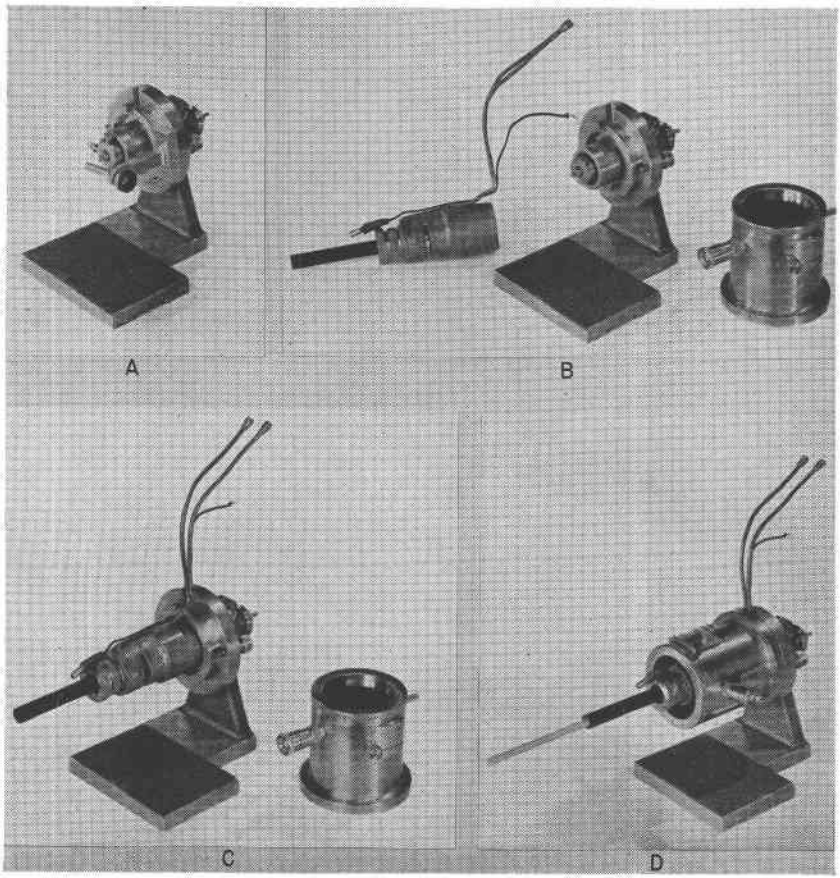


FIG. 5

Specimen-Holding and Centering Device. The specimen is prepared by the method of Buerger[15] or by the method described by Lukesh,[16] or, in certain instances, is sealed within a glass capillary. The metal specimen holder is placed in a centering chuck which differs from that used in the ordinary powder camera by having removable adjusting knobs, Fig. 5*A*.[17] These are really small screwdrivers (outer knobs) which are held in place on the chuck by taper plugs (inner knobs). These screw drivers are plugged in during centering operations and removed when this is completed so that the chuck and specimen can be retracted for reasons mentioned below.

A great convenience in centering the specimen is a detachable "microscope." This is arranged to fit during centering operations on the same base which holds the camera unit during the exposure, as shown in Fig. 5*A*. It consists principally of a lens at the end of a brass tube of fine bore. The lens is located at a distance from the specimen equal to its focal distance.[18] When looking at the specimen through this system, the eye sees the specimen framed in the aperture at the far end of the tube. Before adjustment, the specimen, when rotated, usually appears to move up and down in this aperture. By adjusting the milled knobs of the screwdrivers, the specimen is caused to become concentric with the axis of rotation, after which it appears to remain stationary in the aperture of the microscope when the shaft is rotated.

When the specimen adjustment has been accomplished, the following changes in the apparatus setup are made, in this order:

(1) The microscope is removed by unscrewing the milled nut shown at the right of Fig. 5*A*.

(2) The screwdriver adjusters for the specimen centering device are removed as follows: The outer, screwdriver handles are pulled outward to disengage them and thus avoid spoiling the adjustment. Then the taper plugs are removed by pulling on the inner knobs with a rotating motion. The apparatus then appears as in Fig. 5*B*.

(3) The specimen is retracted into the hollow central hub of the camera base by pulling the shaft and pulley to the right. This protects the specimen while attaching the furnace unit.

(4) The furnace, Fig. 5*B*, left, is slipped onto the central hub of the camera holder in such a way that the non-grounded wire and the cooling water leads fit into the recess in the camera base. The apparatus then appears as shown in Fig. 5*C*.

(5) The shaft and pulley are pushed back so that the specimen enters the small axial hole in the furnace. A recoverable final position for the specimen is assured by the following arrangement: The specimen shaft has a small circumferential groove turned into it at a

[15] Buerger, *op. cit.*, p. 16.

[16] Lukesh, Joseph S., An improved technique for mounting powdered samples for x-ray diffraction: *Rev. Sci. Instruments*, **11**, 200–201 (1940).

[17] Buerger, *op. cit.*, p. 14.

[18] Buerger, M. J., The precision determination of the linear and angular lattice constants of single crystals: *Zeits. Krist.*, (A) **97**, 441 (1937).

convenient place which normally lies within the bearing. The shaft is normally retained in this place by a small ball which lies in the bottom of a transverse drillhole in the bearing. When the shaft is translated out of position as in (3) and then restored, the ball falls into the groove in the shaft when the shaft reaches the correct position and prevents the shaft from moving axially. The ball is maintained against the shaft by means of a weak spring

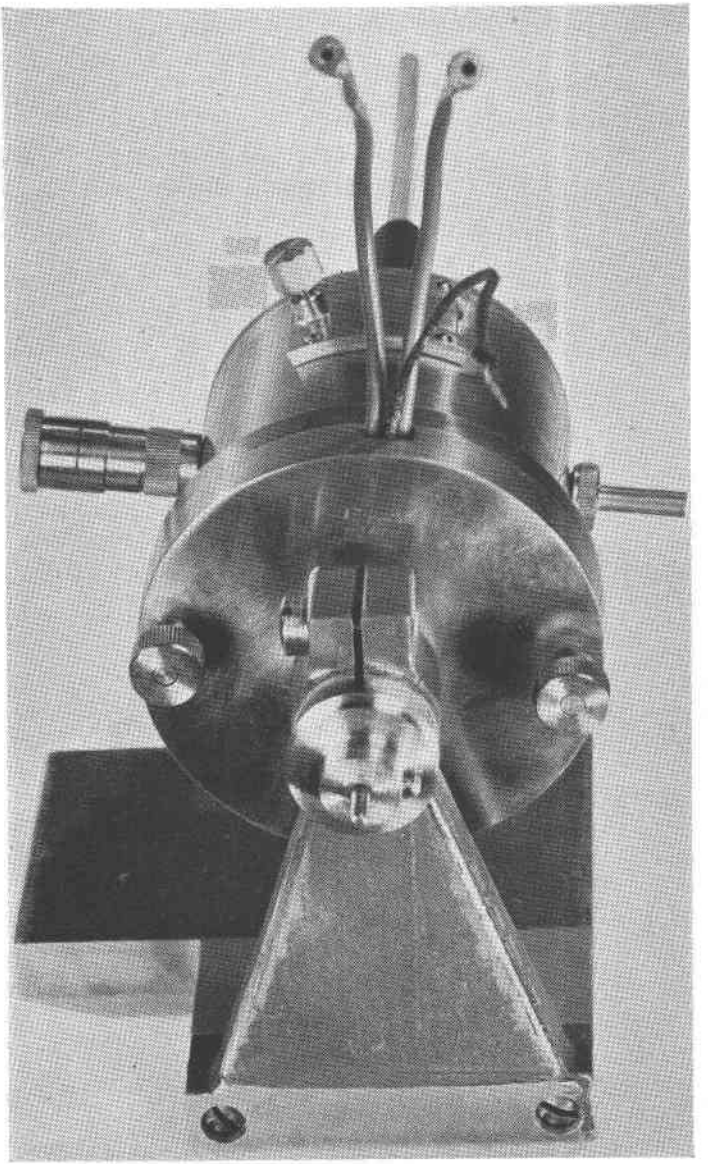


FIG. 6

(6) The loaded camera described below is slipped into a circular base, and fixed firmly in this position by tightening the milled knob shown in Fig. 6. The final appearance of the assembled apparatus is shown in Fig. 5*D*.

The Camera Unit. The camera proper has been deliberately designed so that it can be removed for development and replacement of the film while the specimen remains undisturbed in the furnace. This permits controlling the heat treatment of the specimen independently of making an x-ray photograph of its condition.

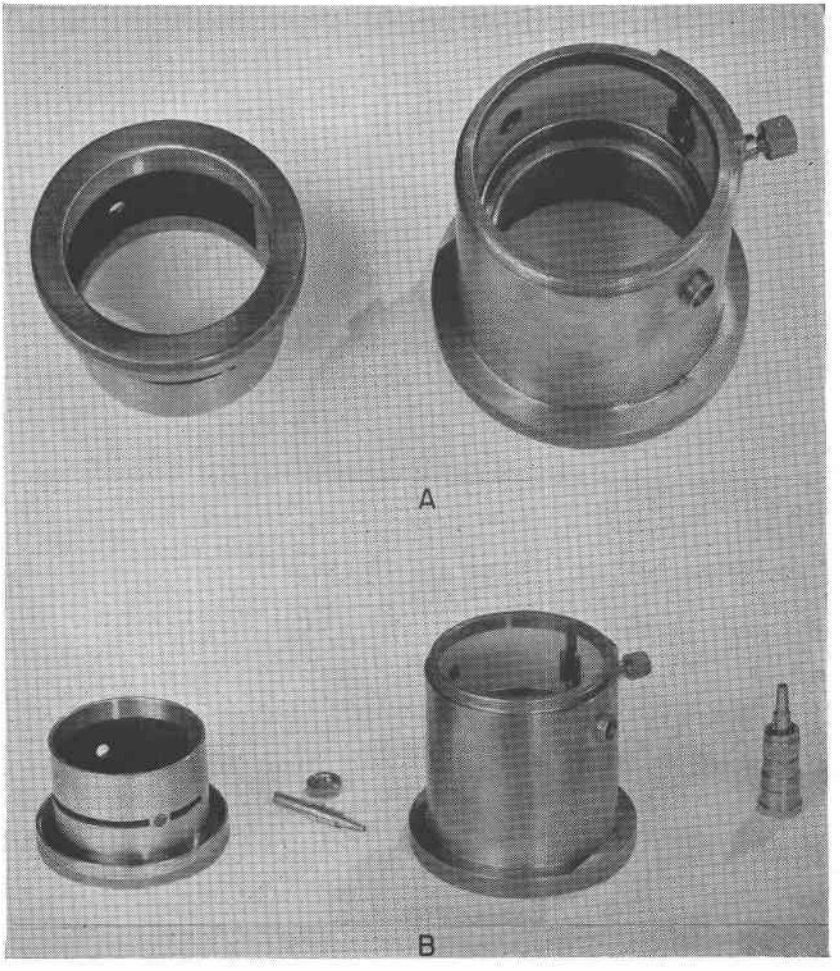


FIG. 7

The assembled camera unit for the 57.3 mm. diameter camera is shown at the right of Fig. 5*B*. Figure 7 shows this unit dismounted for the removal of the film. The film is placed in the camera Straumanis-fashion.[19,20] The reason for this is not so much to utilize Straumanis' strategy for determining the camera diameter, as to place the ends of the film in a position of a desirable blind spot (above the nonslotted part of the heating unit, Figs. 5*C* and 4). The furnace unit must have a blind spot, and this particular position permits having one continuous film record of reflections from $2\theta = 0°$ to $2\theta = 180°$. This position also provides a doubled record in the back reflection field so that the Bradley and Jay[21] strategy for refining lattice constants can be used and at the same time shrinkage errors can be completely eliminated as described by Cohen.[22,23,24]

The film is spread against the inside of the brass camera drum by means of a pair of claws, one fixed and the other movable. The inside of this device is shown in Fig. 7*A*, and the outside in Fig. 5*D*. In loading, the film is placed somewhat loosely in the camera and then the spreader is operated and locked in the spread position. This automatically centers the film so that the holes for entrance and exit of the *x*-ray beam come accurately to position opposite corresponding holes in the camera cylinder. The film holes are neatly punched with a device which simultaneously cuts a 1×7 inch strip from a standard 5×7 inch double coated *x*-ray film.

After the film is in position, it is protected from light by slipping within the camera drum, another drum (left of Fig. 7*A*) which covers the film. The cover of this drum screws into the top of the film-holding drum and at the same time the bottom of the inside drum fits into a recess in the film-holding drum. The latter arrangement acts as a light-maze and prevents fogging of the film. The diffracted *x*-rays reach the film through a slit in the inner drum, Fig. 7*B*, and light is prevented from using the

[19] Straumanis, M., and Ieviņš, A., Präzisionsbestimmung von Glanzwinkeln und Gitterkonstanten nach der Methode von Debye und Scherrer: *Naturwissenschaften*, **23,** 833 (1935).

[20] Straumanis, M., and Ieveņš, A., Präzisionsaufnahmen nach dem Verfahren von Debye und Scherrer. II: *Zeit. Physik*, **98,** 461, 462, 466 (1936).

[21] Bradley, A. J., and Jay, A. H., A method of deducing accurate values of the lattice spacing from *x*-ray powder photographs taken by the Debye-Scherrer method: *Proc. Phys. Soc.*, **44,** 563–579 (1932).

[22] Cohen, M. U., Precision lattice constants from *x*-ray powder photographs: *Rev. Sci. Instruments*, **6,** 68–74 (1935); **7,** 155 (1936).

[23] Cohen, M. U., The elimination of systematic errors in powder photographs: *Zeits. Krist.*, (A) **94,** 288–298 (1936).

[24] Cohen, M. U., The calculation of precise lattice constants from *x*-ray powder photographs: *Zeits. Krist.*, (A) **94,** 306–310 (1936).

same path by covering the slit with black paper. The light-tightness of the film chamber is finally made complete by inserting the entrance port, (which is the pinhole system), and the exit port, Fig. 7*B*. These are both turnings with shelves in such positions as to form light-mazes with the drums.

The exit port has a number of functions. Besides permitting the beam to leave the camera, it envelopes the *x*-ray beam path on the exit side of the specimen in the camera and thus prevents *x*-rays scattered by the air along the beam path from reaching the film. The end of the port is fitted with a disk of fluorescent screen which permits the operator to check the adjustment of the pinhole system and specimen in the *x*-ray beam at any time. The operator is protected from the *x*-ray beam by a disk of lead glass at the end of the exit port.

The entire camera unit, Fig. 5*B*, right, fits against its circular base in such a way as to recover exact position each time. This is assured by accurate concentricity of the two turnings. The camera is held in place against the base by means of a couple of non-removable screws with milled handles, shown in Fig. 6. The assembled camera is shown in Figs. 1 and 5*D*.

Operation of the Furnace. The temperature of the furnace is regulated by connecting the heating coil in series with a slide wire rheostat for coarse adjustment and a carbon-block rheostat for fine adjustment. Satisfactory operation cannot be achieved by connecting this electrical sequence directly to a 110-volt power supply, for experience has shown that the ordinary power source is much too variable to maintain a constant temperature in the furnace. (A voltage stabilizer might be used to improve the voltage constancy of such a source.) We solved the problem of a constant source by utilizing storage batteries. With the apparatus described, one 6-volt storage battery is sufficient for operating at temperatures up to about 200° C. and two batteries in series are sufficient for temperatures up to about 600° C. For phase diagram work, we keep an equal number of batteries constantly charging, and change batteries every 24 hours of continuous run. When the change is made, care must be taken to watch the output drop in the battery during the first hour after charging. By the end of this time, its output approaches sufficient constancy until the battery approaches exhaustion, and the temperature of the furnace can be maintained constant to within about a degree.

Calibration of Furnace Temperatures. It might be supposed that the temperature of the furnace could be adequately determined with the aid of a thermocouple. Unfortunately this is not the case; a thermocouple always indicates too low a reading, as determined by the more accurate method described beyond. This is due to the fact that the tiny furnace does not

heat the entire thermocouple, but only the junction; consequently the thermocouple leads, which are colder than the junction, conduct this tiny amount of heat away rapidly, lowering the temperature of the thermocouple junction below that actually supplied by the furnace. The position of the thermocouple, if used, is shown in Fig. 5*D*.

Our method of calibration is to make use of polymorphism. If a crystalline substance which exhibits a polymorphic transition of the rapid variety is used as the specimen, the temperature is known at which its x-ray pattern changes. If the electrical energy supplied to the furnace windings to obtain two x-ray patterns, one on each side of the polymorphic change, is recorded, then some energy reading between these corresponds with the known temperature of the polymorphic change.

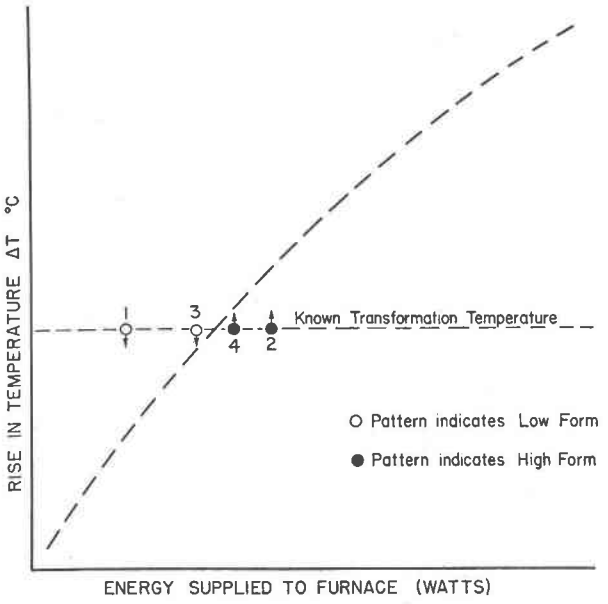


FIG. 8

Figure 8 illustrates the technique of determining the minimum energy supplied to the furnace sufficient to bring about the transformation. The trials are numbered 1, 2, 3, and 4. A photograph is first made with the specimen maintained at an energy setting 1; suppose that the pattern proves to be that of the low form. A higher energy setting 2, is then tried; the pattern then proves to be that of the high form. The true energy required for the transformation temperature, therefore, lies between readings 1 and 2. Adjustments are then made to give an energy reading,

3, halfway between readings 1 and 2. Suppose that the photograph proves that the crystal is now in the low form. The correct energy reading for the transformation then lies between readings 2 and 3. The rheostats are therefore set to give a reading 4, halfway between these. The photograph proves that the crystal has now transformed to the high form and therefore the correct energy reading for the transformation temperature lies between readings 3 and 4. This process can be continued so that this energy difference is refined as close as desired within the range of constancy of the furnace temperature and within the temperature hysteresis of the transformation.

When several such points have been determined, a smooth curve may be drawn relating the electrical input of the furnace to its temperature rise, called ΔT in Fig. 9. ΔT is the temperature rise above the cooling water temperature (which form a base level for temperature rises). The base level temperature is measured by means of a thermometer in the cooling water inlet, Fig. 10.

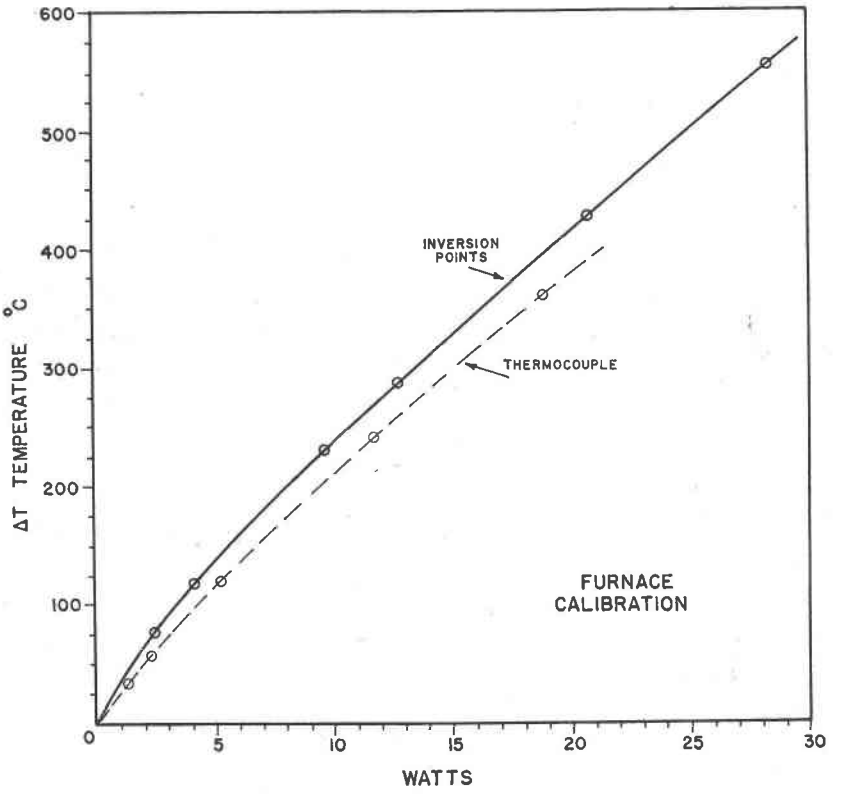


FIG. 9

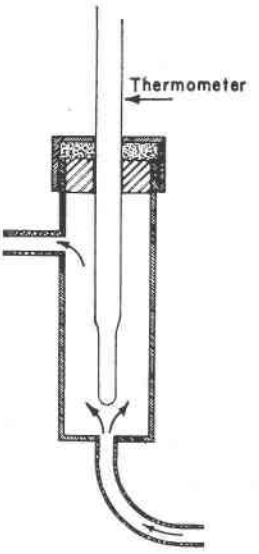


FIG. 10

Mr. Joseph Lukesh[25] has found emperically that if this relation is plotted on log-log graph paper, it can be represented by a straight line. This greatly aids in both interpolation between calibrated values and extrapolation. The relation between input voltage to the furnace and temperature rise has the general form:

$$\Delta T = kV^a.$$

The approximate values for the powder camera here described and the Weissenberg camera mentioned beyond are:

Powder camera	Weissenberg camera
$\Delta T \cong 22\ V^{1.17}$	$\Delta T \cong 10.5\ V^{1.71}$

A rough analysis of the relation between temperature and power input for the two furnaces shows that:

Powder camera	Weissenberg camera
$\Delta T \propto P^{0.60}$	$\Delta T \propto P^{0.85}$

If the heat losses were completely due to radiation, then $\Delta T \propto P^{0.25}$, assuming the furnace temperature is considerably higher than that of the surroundings; and if they were completely due to conduction then $\Delta T \propto P^{1.0}$. The furnace in the Weissenberg camera evidently has a greater conduction loss than that in the powder camera. This can be accounted

[25] Personal communication.

TYPICAL INVERSIONS USED FOR CALIBRATION

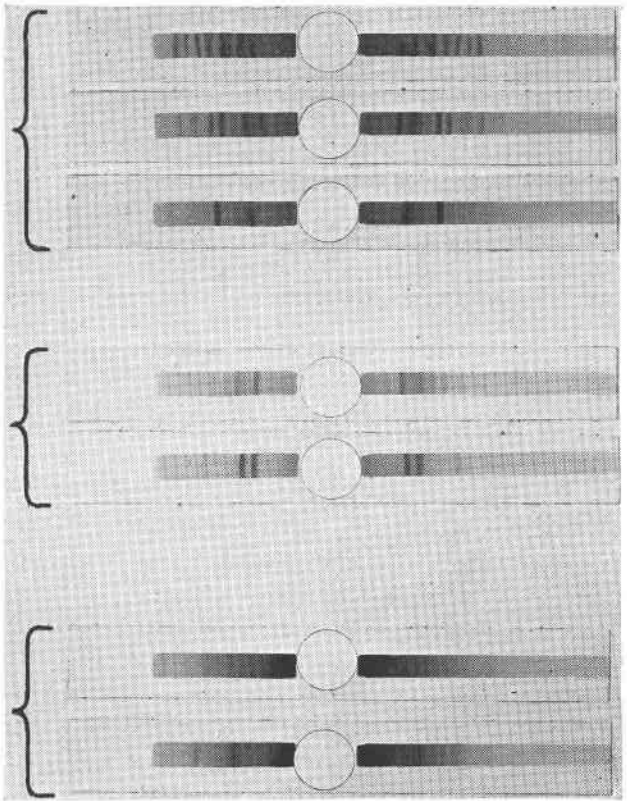
Substance	Pattern	Form	Temperature
NH_4NO_3		Orthorhombic	
			85.4
		Tetragonal	
			126.2
		Cubic	
NH_4ClO_4		Orthorhombic	
			236.5
		Cubic	
$KClO_4$		Orthorhombic	
			295.7
		Cubic	

FIG. 11

for by the presence of a wider slot in the Weissenberg camera to accommodate facilities for equi-inclination procedures, other things being equal.

X-ray patterns of certain desirable substances showing polymorphism of a character useful in calibration are shown in Fig. 11. To this list may be added quartz, whose high-low transformation occurs at 573° C.

Adaptation to Weissenberg Technique. The above described heating unit with slight modification has been adapted to a Weissenberg[26] camera. In this adaptation, the heating chamber is built into a tube which slips over the spindle housing of the Weissenberg. This arrangement in no way interferes with the normal flexibility of the Weissenberg and it has been successfully used in the study of high chalcocite[27] and high tridymite.[28] It is hoped that a more detailed description of this apparatus will be published subsequently.

[26] Buerger, Newton W., Weissenberg controlled-temperature technique: *Am. Mineral.*, **27**, 217 (1942).

[27] Buerger, M. J., and Buerger, Newton W., Structural relations between high- and low-chalcocite: *Am. Mineral.*, **27**, 216 (1942).

[28] Buerger, M. J., and Lukesh, Joseph S., The tridymite problem: *Science*, **95**, 21 (1942).