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NATIONAL BUREAU OF STANDARDS REPORT

7466

THERMAL CONDUCTIVITY OF SEMICONDUCTIVE SOLIDS;
METHOD FOR STEADY-STATE MEASUREMENTS ON
SMALL DISK REFERENCE SAMPLES

Technical Progress Report
for Period
October 1 to December 31, 1961

by

D. R. Flynn

Report to the
Bureau of Ships
Department of the Navy
Washington, D. C.

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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The functions of the National Bureau of Standards are set forth in the Act of Congress, March 3, 1901, as amended by Congress in Public Law 619, 1950. These include the development and maintenance of the national standards of measurement and the provision of means and methods for making measurements consistent with these standards; the determination of physical constants and properties of materials; the development of methods and instruments for testing materials, devices, and structures; advisory services to government agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; and the development of standard practices, codes, and specifications. The work includes basic and applied research, development, engineering, instrumentation, testing, evaluation, calibration services, and various consultation and information services. Research projects are also performed for other government agencies when the work relates to and supplements the basic program of the Bureau or when the Bureau's unique competence is required. The scope of activities is suggested by the listing of divisions and sections on the inside of the back cover.

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A complete listing of the Bureau's publications can be found in National Bureau of Standards Circular 460, Publications of the National Bureau of Standards, 1901 to June 1947 ($1.25), and the Supplement to National Bureau of Standards Circular 460, July 1947 to June 1957 ($1.50), and Miscellaneous Publication 240, July 1957 to June 1960 (Includes Titles of Papers Published in Outside Journals 1950 to 1959) ($2.25); available from the Superintendent of Documents, Government Printing Office, Washington 25, D. C.

NATIONAL BUREAU OF STANDARDS REPORT

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Heat Transfer Section
Building Research Division

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Thermal Conductivity of Semiconductive Solids; Method for Steady-State Measurements on Small Disk Reference Samples

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1. ABSTRACT

Thermal conductivity measurements were conducted over the temperature range 200° to 1200°C on a specimen of Inconel 702 (79.3% Ni, 17% Cr, 2.5% Al). The results plot smoothly from 0.142 w/cm C at 200°C to 0.341 w/cm C at 1200°C and are in excellent agreement with previous NBS determinations for this material.

2. STATEMENT OF PURPOSE

To develop a method and apparatus for steady-state thermal conductivity measurements at temperatures to 800°C and above, and suitable for solids in the form of small specimens (1/2-in. by 1-in. diameter disks), with the objective of providing samples for use by other laboratories as thermal conductivity reference specimens in connection with their measurements on solid semiconductors.

3. WORK PERFORMED IN REPORTING PERIOD (October 1 to December 31, 1961)

During this quarter measurements were made of the thermal conductivity of a specimen of nickel-chromium alloy (Inconel 702). The specimen was in the form of a right cylinder 2.54 cm in diameter and 7.62 cm in length, which was machined from the same solution-annealed hot-rolled plate as were specimens previously measured in two models of the NBS metals apparatus, in the NBS modified prototype absolute cut-bar apparatus, and in the NBS steam calorimeter apparatus. Since the thermal conductivity of this alloy is believed to be well known (±2%) over a large temperature range, measurements on this material should enable confirmation of the accuracy of the high temperature absolute cut-bar apparatus.

Measurements were made over the temperature range 200° to 1200°C in the high temperature model of the absolute cut-bar apparatus. (For a description of this equipment, see

NBS Report 7323.) The specimen was supported between the alumina tube below and the alumina rod above. The thermal insulation used throughout the apparatus was alumina powder. The power generated in the specimen heater was determined by current and potential drop measurements, using a calibrated volt box and shunt box in conjunction with a precision potentiometer.

The temperature distribution along the nickel-chromium specimen was determined by means of four butt-welded platinum: platinum-10% rhodium thermocouples, fabricated from calibrated 0.38 mm reference grade wire, pressed into four transverse 0.3 mm grooves in the convex surface of the bar. Each of the four specimen thermocouples could be read against an ice junction, so that temperature gradients could be determined by difference.

The insulated room-temperature zone box was wired to enable determination of the emf developed between similar leads of different thermocouples. The emf was measured between the platinum wires of the lower two thermocouple junctions in the specimen, the platinum wires of the upper two junctions, the platinum-10% rhodium wires of the lower two junctions, and the platinum-10% rhodium wires of the upper two junctions. Thus, the nickel-chromium alloy bar served as the central portion of four differential thermocouples. These measurements were used as checks of the internal consistency of the platinum:platinum-10% rhodium thermocouples. In addition, they enabled determination of the thermoelectric power of the nickel-chromium alloy vs either platinum or platinum-10% rhodium.

Thermal conductivity measurements were made at 200°C, and in increasing order of temperature at 100 deg C intervals from 400° to 1200°C, and then in decreasing order of temperature at 900°, 600°, and 300°C. Each conductivity determination involved two tests. First, an "isothermal" test, in which there was no power input to the specimen heater, was made to determine variations between specimen thermocouples. This test was followed by a "gradient" test with sufficient power input to the specimen heater to maintain a longitudinal temperature gradient in the specimen of about 4 or 5 deg C/cm. In all of the tests, the guards were adjusted so that there was little net heat exchange between the specimen bar assembly and the surrounding insulation.

A program was developed to enable all data processing and calculations to be effected by means of the IBM 7090 computer facilities installed at NBS during this quarter. The analysis carried out is basically that described in Appendices A and B of the Interim Technical Report Covering Period February 23, 1959, to March 31, 1961 (NBS Report 7135). The major differences are:

a) In the evaluation of heat exchanges between the specimen and the surrounding powder insulation, the analysis has been extended so as to allow for a linear variation of the thermal conductivity of the insulation with temperature.

b) A simultaneous solution of the "gradient" test and the "isothermal" test is carried out by the computer. This tends to minimize the effect of any systematic errors which might be present either in temperature measurements or in heat flow.

c) The thermoelectric power of the specimen vs platinum and vs platinum-10% rhodium is also computed. The results obtained vs platinum-10% rhodium are adjusted, using the known thermoelectric power of platinum-10% rhodium vs platinum, to yield a separate value for the thermoelectric power vs platinum.

Since temperature gradients in the specimen are rather small, it is essential that the conversion of thermocouple emfs to temperature does not introduce any additional uncertainties. The equation

$$E = 16.82614\left(\frac{T}{1000}\right) - 10.30487\left(\frac{T}{1000}\right)^2 + 7.912461\left(\frac{T}{1000}\right)^3 - 2.053050\left(\frac{T}{1000}\right)^4 - 2.853748\left(1.0 - e^{-\frac{4T}{1000}}\right) ,$$

where T is temperature (°C) and E is emf (millivolts), was found to fit the platinum:platinum-10% rhodium thermocouples' calibration data provided by the NBS High Temperature Measurements Laboratory quite closely over the temperature range 0° to 1450°C. This equation was incorporated into the computer program for conversion of all thermocouple voltages to temperature.

The thermal conductivity of the nickel-chromium alloy as determined by simultaneous solution of the various pairs of tests is shown in figure 1. The points plotted are weighted averages of the values obtained in each pair of tests for the three thermocouple spans. Due to uncertainty in the effective distances between thermocouples, there was some scatter in the individual values obtained for each span. The average of the three values, weighted according to the length of each span, retains only about one-third of this uncertainty.

The circles shown in figure 1 represent measurements made in increasing order of temperature, and the inverted triangles those made in decreasing order of temperature. The solid line shown is the cubic equation of least-mean-squares fit to all of the data points represented by circles. This equation is

$$k=0.1198+0.07387\left(\frac{T}{1000}\right)+0.1915\left(\frac{T}{1000}\right)^2-0.08265\left(\frac{T}{1000}\right)^3 \quad ,$$

where T is temperature (°C) and k is thermal conductivity.

To enable closer scrutiny of the deviation of individual determinations from the curve, these are shown in figure 2 as percent departures from the smooth curve plotted against temperature. The dotted lines bound the region plus and minus two standard deviations from the solid line. The maximum departure from the solid line of any point represented by a circle is 0.6 percent. The inverted triangles depart significantly from the solid line as the temperature decreases, being high by 1.1 percent at 600°C and by 3.2 percent at 300°C. It is believed these two departures reflect an actual change in the specimen conductivity rather than measurement error. Inconel 702 is reported to age-harden if held for 4 hours at temperatures around 730°C. It would not be surprising to detect a change in thermal conductivity at lower temperatures after the specimen had passed slowly through this temperature range, as it did in the decreasing-temperature tests.

The smoothed results of this determination are tabulated in the second column of table 1 at 100 deg C intervals over the temperature range 200° to 1200°C. Results obtained by several other methods on specimens cut from the same plate of nickel-chromium alloy are included in table 1 for comparison. The data presented in the third column were obtained by means of the modified prototype absolute cut-bar and are discussed in detail in NBS Report 7135. The tabulated values are those from the quadratic equation of least-mean-squares fit through data points for peened thermocouples only. The data in the fourth column represent the manually smoothed data from numerous runs on two specimens of the alloy in two models of the NBS metals apparatus [1]. The fifth column presents data obtained on a specimen six inches in diameter and one inch thick in the NBS steam calorimeter apparatus. The tabulated values correspond to the linear equation of least-mean-squares fit to the calorimeter data available as of this date. With the exception of one point (steam calorimeter at 600°C) the thermal conductivity values tabulated in table 1 are within ±1 percent of their mean value at any given temperature.

Since all of the results presented in table 1 are from this laboratory, results obtained on similar alloys by an independent laboratory may also be of interest. Powell and Tye of the National Physical Laboratory recently reported a series of measurements on a group of nickel-chromium alloys somewhat similar in composition to the alloy being investigated at NBS. The chemical composition of the NBS alloy is presented in table 2 along with the composition of three of the NPL alloys. Table 3 presents tabulated thermal conductivity values for the NBS alloy as determined by this investigation and for the NPL alloys as reported [2]. Inspection of table 3 reveals that the thermal conductivity values for the four alloys have a range, at any given temperature, of about 13 percent at the lower temperatures and that the values converge at higher temperatures such that the range at 800°C is only 3 percent. The data acquired at NBS for Inconel 702 show a slightly larger increase with temperature than do the NPL results for Nimonic alloys. As noted above, this may be partly due to different thermal histories.

The results of the tests made to date in the high temperature absolute cut-bar apparatus serve as an indication of the precision and accuracy possible with this apparatus. It is felt that measurements can soon begin on materials having thermal conductivity similar to those of thermoelectric materials of interest.

4. FUTURE ACTIVITIES

Additional measurements will be made on the specimen of Inconel 702 to determine if the thermal conductivity at lower temperatures was actually changed by heat treatment. Such measurements are considered necessary to establish the ability of the high temperature absolute cut-bar apparatus to reproduce results after operation at high temperatures.

Initial measurements on lower conductivity material will be undertaken soon on a 1/2-inch by 1-inch diameter disk of Pyroceram 9606. Thermal conductivity measurements on Pyroceram 9606 were made in the modified prototype absolute cut-bar apparatus and are currently underway in the NBS metals apparatus. Thermal diffusivity determinations are being made at NBS by the Heat Measurements Section. This material was chosen as having a thermal conductivity similar to that of many thermoelectric materials. Preliminary results indicate that it may be an excellent reference material.

A series of tests will be made with the Pyroceram 9606 specimen to evaluate the effects of heat exchanges with the insulation and of thermal contact resistance. Following the completion of tests on Pyroceram 9606, measurements will be undertaken on selected thermal conductivity reference samples provided by the Bureau of Ships.

Work will be begun soon on an annual report describing activities since April 1, 1961. The report will present much more technical detail concerning the high temperature absolute cut-bar apparatus than has previously been given.

5. REFERENCES

[1]. "Thermal Conductivity of Some Commercial Iron-Nickel Alloys," by T. W. Watson and H. E. Robinson, Trans. of the ASME Jour. of Heat Transfer, November 1961, pp. 403-408.

[2]. "Thermal and Electrical Conductivities of Nickel-Chromium (Nimonic) Alloys," by R. W. Powell and R. P. Tye, The Engineer, April 29, 1960, pp. 729-732.

TABLE 1

Thermal Conductivity of a Nickel-Chromium Alloy (Inconel 702) by Several Independent Methods at NBS

Temp., °C	This Investigation	Prototype Absolute Cut-Bar	Metals Apparatus	Steam Calorimeter
-100	-----	-----	0.103	-----
0	-----	-----	.114	-----
100	-----	-----	.127	-----
200	0.142	0.142	.142	-----
300	.157	.159	.158	-----
400	.175	.177	.176	-----
500	.194	.197	.196	-----
600	.215	.217	.218	0.213
700	.237	.238	-----	.235
800	.259	.260	-----	.258
900	.281	-----	-----	.280
1000	.303	-----	-----	.303
1100	.323	-----	-----	-----
1200	.341	-----	-----	-----

TABLE 2

Chemical Compositions of Four
Nickel-Chromium Alloys

	Composition, weight percent									
	Cr	Al	Ti	Fe	Si	Cu	Co	Mn	C	Ni
NBS Alloy	17.0	2.5	0.59	0.36	0.19	0.14	0.08	0.04	0.066	79.3
Nimonic 75	20.53	----	0.23	0.12	0.79	0.06	-----	0.27	0.126	77.9**
Nimonic 80*	21.0	1.2	2.5	0.5	0.5	----	-----	0.6	0.04	73.7**
Nimonic 90	19.5	1.40	2.45	0.41	0.65	0.14	16.5	0.03	0.06	58.9**

*Nominal Composition
**By Difference

TABLE 3

Thermal Conductivity of Four
Nickel-Chromium Alloys

Temp., °C	NBS Inconel 702	NPL Nimonic 75	NPL Nimonic 80	NPL Nimonic 90
200	0.142	0.157	0.138	0.146
300	.157	.175	.155	.165
400	.175	.191	.168	.184
500	.194	.210	.184	.200
600	.215	.226	.210	.218
700	.237	.243	.235	.237
800	.259	.260	.255	.253
900	.281	-----	.276	-----

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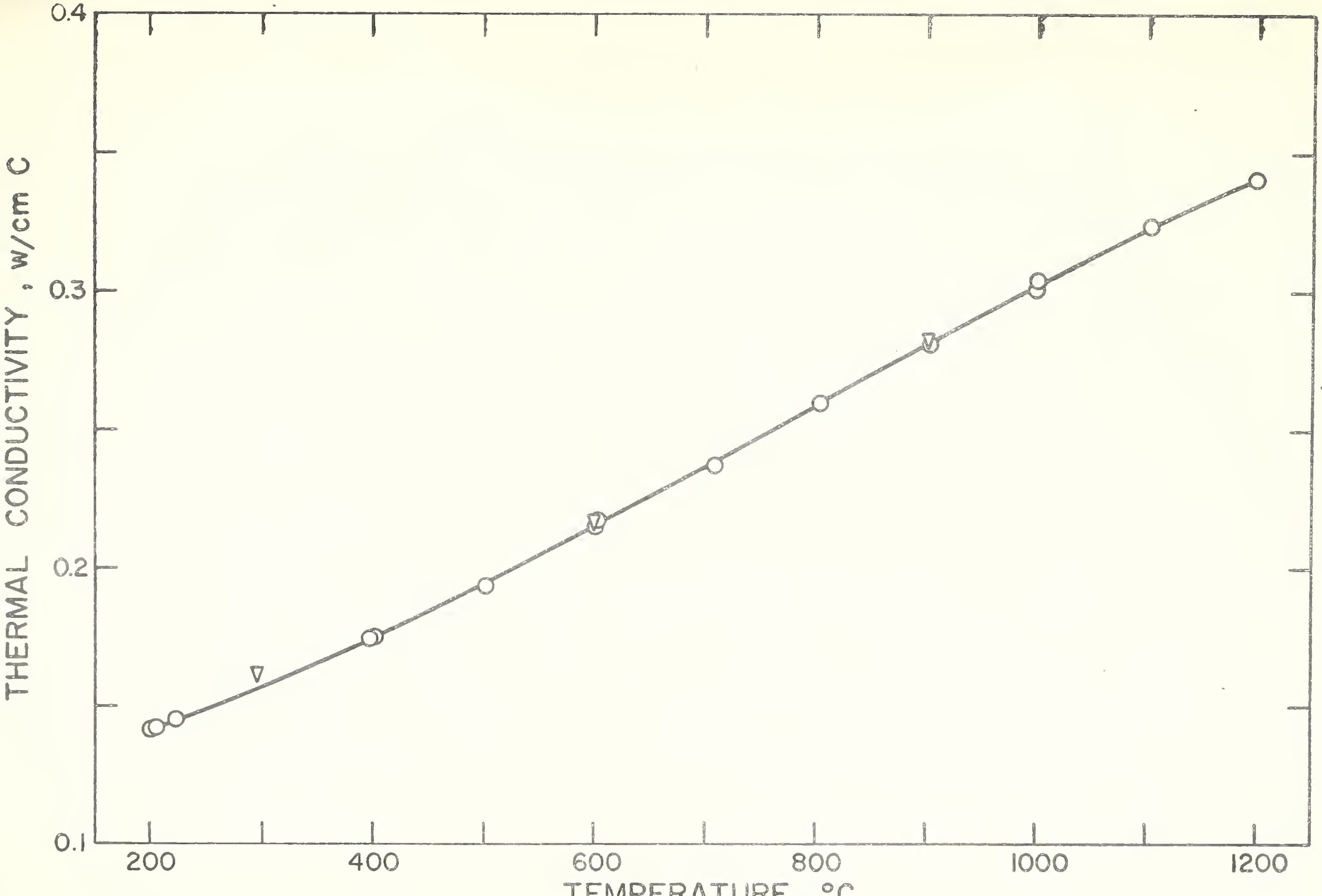

Fig. 1. Thermal conductivity of Inconel 702 as determined by the high temperature absolute cut-bar apparatus.

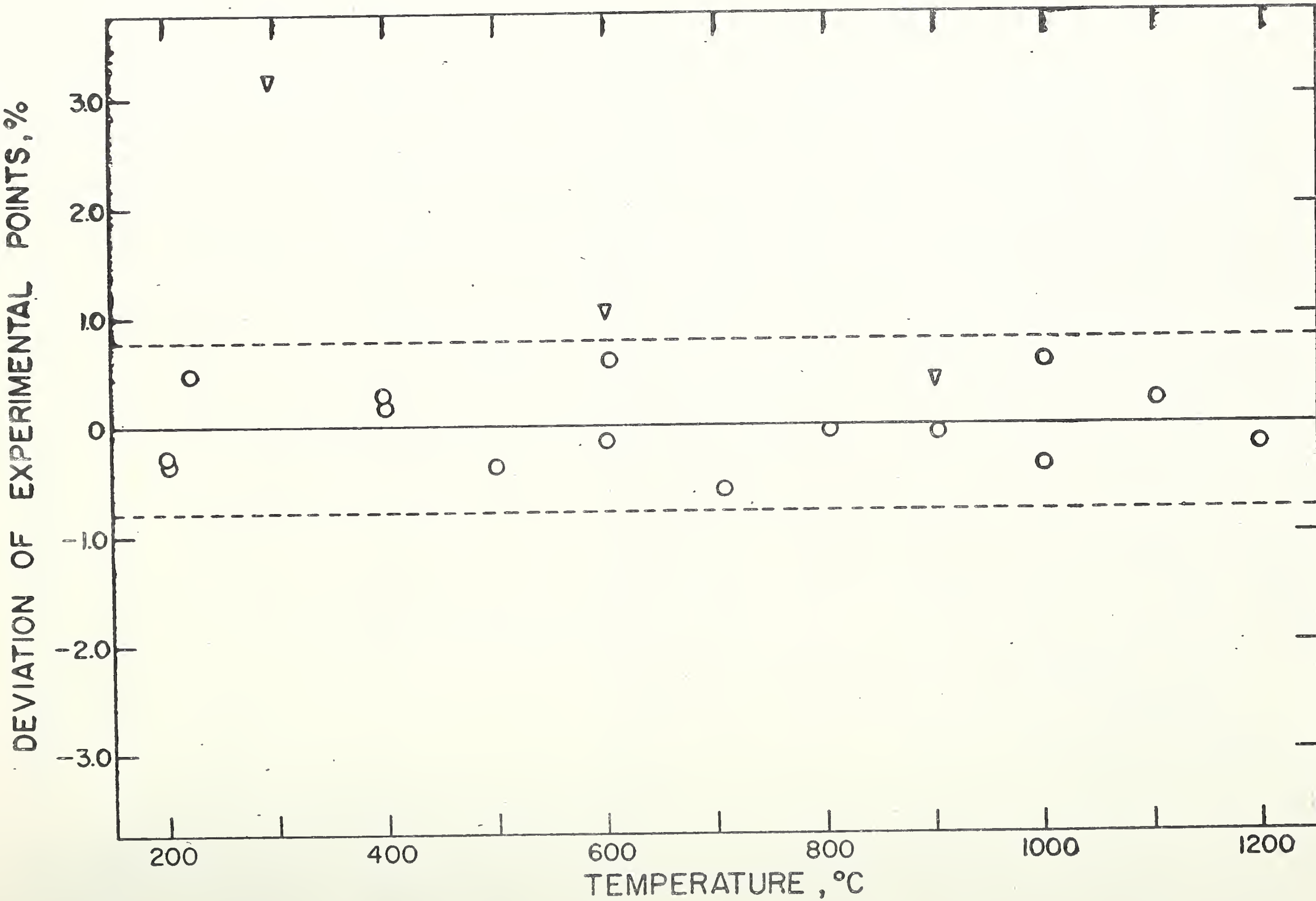

Fig. 2. Departures of the data in figure 1 from a smooth curve.

U. S. DEPARTMENT OF COMMERCE
Luther H. Hodges, *Secretary*

NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

WASHINGTON, D.C.

Electricity. Resistance and Reactance. Electrochemistry. Electrical Instruments. Magnetic Measurements. Dielectrics. High Voltage.

Metrology. Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Scale. Volumetry and Densimetry.

Heat. Temperature Physics. Heat Measurements. Cryogenic Physics. Equation of State. Statistical Physics.

Radiation Physics. X-ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. Nucleonic Instrumentation. Neutron Physics.

Analytical and Inorganic Chemistry. Pure Substances. Spectrochemistry. Solution Chemistry. Standard Reference Materials. Applied Analytical Research.

Mechanics. Sound. Pressure and Vacuum. Fluid Mechanics. Engineering Mechanics. Rheology. Combustion Controls.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastics. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics. Electrolysis and Metal Deposition.

Mineral Products. Engineering Ceramics. Glass. Refractories. Enameled Metals. Crystal Growth. Physical Properties. Constitution and Microstructure.

Building Research. Structural Engineering. Fire Research. Mechanical Systems. Organic Building Materials. Codes and Safety Standards. Heat Transfer. Inorganic Building Materials.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics. Operations Research.

Data Processing Systems. Components and Techniques. Computer Technology. Measurements Automation. Engineering Applications. Systems Analysis.

Atomic Physics. Spectroscopy. Infrared Spectroscopy. Solid State Physics. Electron Physics. Atomic Physics.

Instrumentation. Engineering Electronics. Electron Devices. Electronic Instrumentation. Mechanical Instruments. Basic Instrumentation.

Physical Chemistry. Thermochemistry. Surface Chemistry. Organic Chemistry. Molecular Spectroscopy. Molecular Kinetics. Mass Spectrometry.

Office of Weights and Measures.

BOULDER, COLO.

Cryogenic Engineering. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Cryogenic Technical Services.

Ionosphere Research and Propagation. Low Frequency and Very Low Frequency Research. Ionosphere Research. Prediction Services. Sun-Earth Relationships. Field Engineering. Radio Warning Services. Vertical Soundings Research.

Radio Propagation Engineering. Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation-Terrain Effects. Radio-Meteorology. Lower Atmosphere Physics.

Radio Standards. High Frequency Electrical Standards. Radio Broadcast Service. Radio and Microwave Materials. Atomic Frequency and Time Interval Standards. Electronic Calibration Center. Millimeter-Wave Research. Microwave Circuit Standards.

Radio Systems. Applied Electromagnetic Theory. High Frequency and Very High Frequency Research. Modulation Research. Antenna Research. Navigation Systems.

Upper Atmosphere and Space Physics. Upper Atmosphere and Plasma Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.

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