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THERMAL AND ELECTRICAL CONDUCTIVITIES AND SEEBECK COEFFICIENTS OF UNIRRADIATED AND IRRADIATED GRAPHITES FROM 300 TO 1000 K[a]

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ABSTRACT

The thermal conductivity, λ, electrical resistivity, ρ, and absolute Seebeck coefficient, S, of two grades of nearly isotropic graphite were measured from 300 to 1000 K both before and after neutron irradiation up to 5.0×10^{21} n/cm^2 (>50 KeV). Nominal irradiation temperatures were 823, 923, and 1023 K. The thermal resistance, λ^{-1}, of the unirradiated graphites was proportional to T from 500 to 1000 K. Neutron irradiation decreased λ at 300 K by a factor of 4.5 and increased ρ at 300 K by 2.5, in general agreement with previous investigations, and irradiation changed S from small negative values to large positive ones. The product of thermal conductivity and electrical resistivity was nearly constant with fluence from 2.6×10^{21} to 5.0×10^{21} n/cm^2.

INTRODUCTION

Graphite is an extremely important material with numerous engineering applications, and this is partly due to the diversity of properties that can be obtained to optimize performance. Its hexagonal crystal structure dictates highly anisotropic properties, which are often observed even in fine-grained polycrystalline material from different fabrication techniques (1,2). Nuclear applications often subject graphite to high-energy neutron bombardment, which can have a large effect on the properties. The thermal conductivity, λ, is especially sensitive to irradiation, and this has been the subject of numerous previous investigations, which have been reviewed well by Kelly (3) and by Engle and Eatherly (4).

The purpose of this study was to measure the effects of neutron irradiation at nominal irradiation temperatures of 823, 923, and 1023 K on the λ, the electrical resistivity, ρ, and the absolute Seebeck coefficient, S, of two types of nearly isotropic graphites. The planned procedure was to measure all three properties of the materials before and after irradiation to successively higher fluences, but program shifts prevented work past the first irradiation, and this limits the results.

DESCRIPTION OF SPECIMENS

The graphites studied were AXF-5Q[b] and H-337,[c] with densities of 1.85 and 2.00 g/cm^3, respectively. The Bacon Anisotropy Factor of the AXF-5Q was 1.01 and that of the H-337 was 1.05, thus indicating nearly isotropic materials.

Several 7.8-cm-long cylindrical specimens were cut from a block of each type graphite, and three specimens from each group were selected for study. The selection was based on uniformity of ρ along the length of each specimen and the agreement of ρ among various specimens. The maximum ρ deviation among the three H-337 specimens was 2.6%, and the deviation of ρ along the specimen length from the average ρ was less than ±1.3%. The average ρ of each AXF-5Q specimen was within 2.4% of the other specimens, and the deviation of ρ along the specimen length from the average ρ was less than ±1% in the worst case. The diameters of the specimens varied from 1.13 to 1.22 cm, depending on the desired irradiation temperature.

After λ, ρ, and *S* had been determined for the unirradiated condition, the six specimens were irradiated for two cycles in the High Flux Isotope Reactor (HFIR).[d] The irradiation conditions are given in Table I.

MEASUREMENT TECHNIQUES

The λ, ρ, and *S* of all unirradiated graphites and of irradiated specimens AXF-5Q (823 K), AXF-5Q (923 K), and H-337 (1023 K) were measured in a guarded longitudinal heat flow apparatus, which operated from 300 to 1000 K. A complete description of the technique is given elsewhere (5). The λ was determined by measurements of electrical power dissipated in a heater on one end of the specimen and of the temperature gradient along the specimen with Pt–10% Rh vs Pt thermocouples. The *S*'s were calculated from the voltage drop between platinum thermoelements and the temperature difference between adjacent thermocouples. The ρ's were determined by a standard four-probe direct-current technique.

Thermocouple attachment to the specimens presented a problem since the thermoelements had to be removed for irradiation of the specimens. We drilled 0.0508-cm-diam holes radially through the specimen. A 0.0254-cm-diam platinum wire was then bent back upon itself and pressed into the radial hole on one side of the specimen. A Pt–10% Rh wire of the same configuration and size was pressed into the hole on the other side of the specimen opposite the platinum wire, so that the thermocouple junction was made through the graphite on an isothermal plane. This type contact worked satisfactorily as long as the temperatures at the contact points of the two thermoelements were the same and heat flows along the wires in the vicinity of the wire-specimen contact were small. The latter requirement was ensured by wrapping the insultated wires around the specimen in an isothermal plane and by the presence of a matched guard surrounding the specimen (5).

Irradiated specimen H-337 (823 K) was broken during irradiation capsule disassembly, and this prevented measurement in the above device. However, a small piece of this specimen was salvaged, and the λ and S were measured in another apparatus [apparatus called ORNL-2 by Laubitz and McElroy (6)] from 100 to 400 K.

MEASUREMENT UNCERTAINTIES

The measurement uncertainties were estimated to be less than ±4%, ±5%, and ±0.1 μV/K for ρ, λ, and S, respectively, on the unirradiated graphites. The uncertainty in S increased to ±0.5 μV/K for the irradiated graphites. The large uncertainty in ρ and about one-half that in λ were due to the method of thermocouple wire attachment, which led to uncertainty in thermocouple junction locations.

RESULTS ON UNIRRADIATED GRAPHITES

The thermal resistance, λ^{-1}, of most unirradiated graphites increases as T over a large temperature range; and we have, therefore, plotted λ^{-1} vs T in Fig. 1. Above 500 K, λ^{-1} is linear with T for all specimens measured, and results from the three H-337 specimens agree to within ±2% and those from the two AXF-5Q specimens to within ±1%. This good agreement reflects the homogeneity of the specimens as well as the reproducibility of the measurement technique.

The λ of an AXF-5Q graphite specimen with a ρ at 300 K of 1138 μΩ-cm was not measured before irradiation. Its calculated λ^{-1} based on ρ is presented in Fig. 1 as the dashed line. Since all the AXF-5Q results and all the H-337 results agreed so well, smoothed values of λ have been selected for each material at even temperature intervals, and these are given in Table II.

The S and ρ results from the unirradiated specimens are shown in Fig. 2, and the similarities of the temperature dependences of the two properties are apparent. The scatter of S data about the smooth lines representing the AXF-5Q and the H-337 is within the stated uncertainty of ±0.1 μV/K. All ρ results are within ±1.4% of the curves drawn through the data and this scatter is well below the ρ uncertainty of ±4%. Values taken from the S and ρ curves of Fig. 2 at even temperature intervals are given in Table II.

RESULTS ON IRRADIATED SPECIMENS

Neutron irradiation has an effect on all three properties measured. As shown in Fig. 3, irradiation doubled the electrical resistivities but

did not greatly affect the temperature dependence. The S values change from negative to positive, and their magnitudes increase sharply with irradiation, as shown in Fig. 4. Measurements were not made on the other two irradiated specimens.

The λ results on the irradiated specimens are compared to the unirradiated in Fig. 5. Neutron irradiation reduced λ by a factor of 4.5 near 300 K and by 2.5 near 900 K. The H-337 graphite had the higher λ before irradiation, and even after irradiation to 5.2×10^{21} n/cm^2.

Figure 6 shows the present λ results vs fluence and compares them to other data (7–10). The initial rapid decrease in λ with neutron irradiation is apparent, and it appears that the effect of neutron damage on λ has nearly saturated at some fluence below our lowest value of 2.6×10^{21} n/cm^2. Bridge et al. (11) have indicated that for irradiation temperatures near those of this study, λ should be nearly constant with fluence above 1×10^{21} n/cm^2, and we have taken this into consideration in drawing lines through our results.

DISCUSSION OF RESULTS

In metals and semimetals, λ can be expressed as

$$\lambda = \lambda_e + \lambda_\ell \ , \tag{1}$$

where λ_e is the electronic component due to free charge carriers, and λ_ℓ is the lattice component due to quantized lattice vibrations or phonons. In metals, λ_ℓ is small, and the majority of the heat is carried by the same free electrons responsible for the electrical conductivity. This is the source of the well known Wiedemann-Franz-Lorenz ratio (12).

In graphites, phonons carry most of the heat, and the linear relation observed between λ^{-1} and T is generally attributed to three-phonon umklapp processes, which are dominant in scattering phonons and hence in restricting λ.

Although λ_e of graphites is small, it has been shown experimentally that λ and ρ are related for artificial graphites, and there are as many equations proposed for λ as a function of ρ as there have been investigators. Our 300 K results on the unirradiated graphites are within 8% of the equation

$$\lambda = 1.56 \times 10^{-3}\ \rho^{-1} - 0.266 \times 10^{-6}\ \rho^{-2} \qquad (2)$$

proposed by McElroy et al. (13). This equation represents available data from unirradiated artificial graphites with ρ values between 500 μΩ-cm and 5000 μΩ-cm. The reason for the λ-ρ relation is that the same porosity, grain boundaries, and tortuosity within a specific bulk graphite scatter both phonons and electrons and hence effect both properties. Tyalor et al. (14) have shown that the mean free paths are of the same magnitude.

Equation (2) is not valid for irradiated graphite. The reduction in λ during irradiation at the temperatures of this study is partly due to vacancies (3), which scatter phonons within the basal plane. The ρ is affected similarly in that there are more scattering centers for the charge carriers. However, the introduction of vacancies in the basal planes also shifts the Fermi energy, δ, to another region of the density of states curve, $n(\varepsilon)$, and this has a direct effect on ρ (12, 15).

Matsuo (16) has proposed that the product $\lambda \times \rho$ of graphite irradiated at 575 to 675 K is linear with fluence up to a fluence of 2.2×10^{21} n/cm^2. In Fig. 7 we show $\lambda \times \rho$ vs fluence from Matsuo's work and compare this to our results at greater fluence. It appears that the product of λ and ρ temporarily saturates immediately above the upper fluence of Matsuo's results. This could change, however, at much higher fluence.

The large and positive S's of all the irradiated graphites are particularly interesting. The same vacancies within the graphite basal planes that lower λ and raise ρ also change the sign and magnitude of S by shifting δ to a region on the density of states curve (15, 17), where $dn(\varepsilon)/d\varepsilon$ and, hence, S are large (12). The effect of irradiation on all the properties is similar to that of substitution of boron in carbon sites within the basal plane, although a boron atom is not as effective as is a vacancy. Kelly et al. (18) have shown that the scattering of phonons by vacancy sites is about three times as strong as scattering by substitutional boron. The S of boronated graphite is also positive and large with a maximum of 80 μV/K at a concentration of 0.05% B by weight, and this led to attempts to adapt the material to high-temperature thermocouple use (19). Changes of the Hall coefficient from small negative values to large positive ones have also been noted in graphite after irradiation (17).

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REFERENCES

1. W. N. REYNOLDS, *Physical Properties of Graphites*, Elsevier Publishing Co., Ltd., New York (1968).

2. P. L. WALKER, JR., (Ed.), *Chemistry and Physics of Carbon*, Vol. 5, Marcel Dekker, Inc., New York (1969).

3. B. T. KELLEY, p. 119 in Ref. 2.

4. G. B. ENGLE and W. P. EATHERLY, "Irradiation Behavior of Graphite at High Temperature (A Review)," *High Temp.-High Pressures*, 4, 119 (1972).

5. J. P. MOORE, D. L. McELROY, and R. K. WILLIAMS, report in preparation.

6. M. J. LAUBITZ and D. L. McELROY, "Precise Measurement of Thermal Conductivity at High Temperatures (100–1200 K)," *Metrologia*, 7, 1 (1971).

7. D. E. BAKER, "Thermal Conductivity of Irradiated Graphite by a Rapid Thermal-Pulse Method," *J. Nucl. Mater.*, 12, 120 (1964).

8. R. S. GRAVES, J. P. MOORE, and D. L. McELROY, "Molten-Salt Reactor Program Semiannu. Progr. Rep. Feb. 28, 1969," ORNL-4396, p. 219, Oak Ridge National Laboratory (1969).

9. G. B. ENGLE, and K. KOYAMA, "Thermal Conductivity Changes in Nuclear Graphites at High Temperatures and High Fluences," Gulf-GA-A12137, Gulf General Atomic (June 1972).

10. J. W. HELM, "Irradiation of Graphite at Temperatures of 300 to 1200°C," BNWL-1056A, Battelle Northwest Laboratories (1969).

11. H. BRIDGE, B. T. KELLY, and P. T. NETTLEY, "Effect of High-Flux Fast-Neutron Irradiation on the Physical Properties of Graphite," *Carbon*, 2, 83 (1964).

12. A. H. WILSON, *The Theory of Metals*, 2nd ed., Cambridge University Press (1958).

13. D. L. McELROY, T. G. KOLLIE, W. M. EWING, R. S. GRAVES, and R. M. STEELE, "Room Temperature Measurements of Electrical Resistivity and Thermal Conductivity of Various Graphites," ORNL-TM-3477, Oak Ridge National Laboratory (July 1971).

14. R. TAYLOR, K. E. GILCHRIST, and L. J. POSTON, "Thermal Conductivity of Polycrystalline Graphite," *Carbon*, 6, 537 (1968).

15. A. D. BOARDMAN, M. I. DARBY, and E. T. MICAH, "Density of States in Perturbed Graphite Lattice," *Carbon*, 11, 207 (1973).

16. H. MATSUO, "Relation Between Electrical Resistivity and Thermal Conductivity of Reactor Grade Graphite Irradiated with Neutrons at 300°C–400°C," *J. Nucl. Mater.*, 42, 105 (1972).

17. Y. HISHIYAMA, S. MROZOWSKI, and A. S. VOGH, "Studies of Negative Magnetoresistance in Neutron Irradiated Polycrystalline Graphite and in Boronated Kish Graphite," *Carbon*, 9, 367 (1971).

18. B. T. KELLY, A. WHITTAKER, D. TOBIN, and P. WAGNER, "The Effect of Doping on the Thermal Conductivity of Polycrystalline Graphite," *Carbon*, 9, 447 (1971).

19. C. A. KLEIN and M. P. LEPIE, "Operational Performance Characteristics of Pyrolytic Graphite Thermocouples," *Solid-State Electron.*, 7, 241 (1964).

FOOTNOTES

a. Research sponsored by the U.S. Atomic Energy Commission under Contract with the Union Carbide Corporation.

b. Poco Graphite, Inc., a subsidiary of Union Oil Company of California, P. O. Box 2121, Decatur, Texas 76234.

c. Great Lakes Carbon Corp., 299 Park Avenue, New York, New York 10017.

d. High Flux Isotope Reactor, operated at Oak Ridge National Laboratory.

TABLE I.

Description of Graphite Specimen Irradiations

Temperature of Irradiation (K)	Flux[a] ($n\ cm^{-2}\ sec^{-1}$)	Fluence[a] ($n\ /cm^2$)
823	6.8×10^{14}	2.6×10^{21}
923	10.5	4.2
1023	12.9	5.0

[a] $E > 50$ KeV.

TABLE II.

Thermal Conductivity, Electrical Resistivity, and Absolute Seebeck Coefficient of Unirradiated AXF-5Q and H-337 Graphites

T	AXF-5Q			H-337		
	λ (W cm^{-1} K^{-1})	ρ (μΩ-cm)	S (μV/K)	λ (W cm^{-1} K^{-1})	ρ (μΩ-cm)	S (μV/K)
300		1119	+2.15	1.67	773	+0.35
400	1.22	981	+1.80	1.53	695	−1.30
500	1.11	885	+0.90	1.35	648	−3.70
600	1.01	820	−0.35	1.23	624	−5.75
700	0.93	780	−1.70	1.09	610	−7.4
800	0.85	755	−2.85	1.00	603	−8.3
900	0.79	742	−3.50	0.92	599	−8.55
1000	0.74	730	−3.45	0.85	602	−8.0

LIST OF FIGURES

Fig. 1. Thermal resistance, λ^{-1}, of unirradiated H-337 and AXF-5Q graphites vs T. The ρ values are at 300 K, and the dashed line represents the calculated values based on a ρ at 300 K of 1138 $\mu\Omega$-cm.

Fig. 2. Electrical resistivity and absolute Seebeck coefficient of unirradiated H-337 and AXF-5Q graphite from 300 to 1000 K.

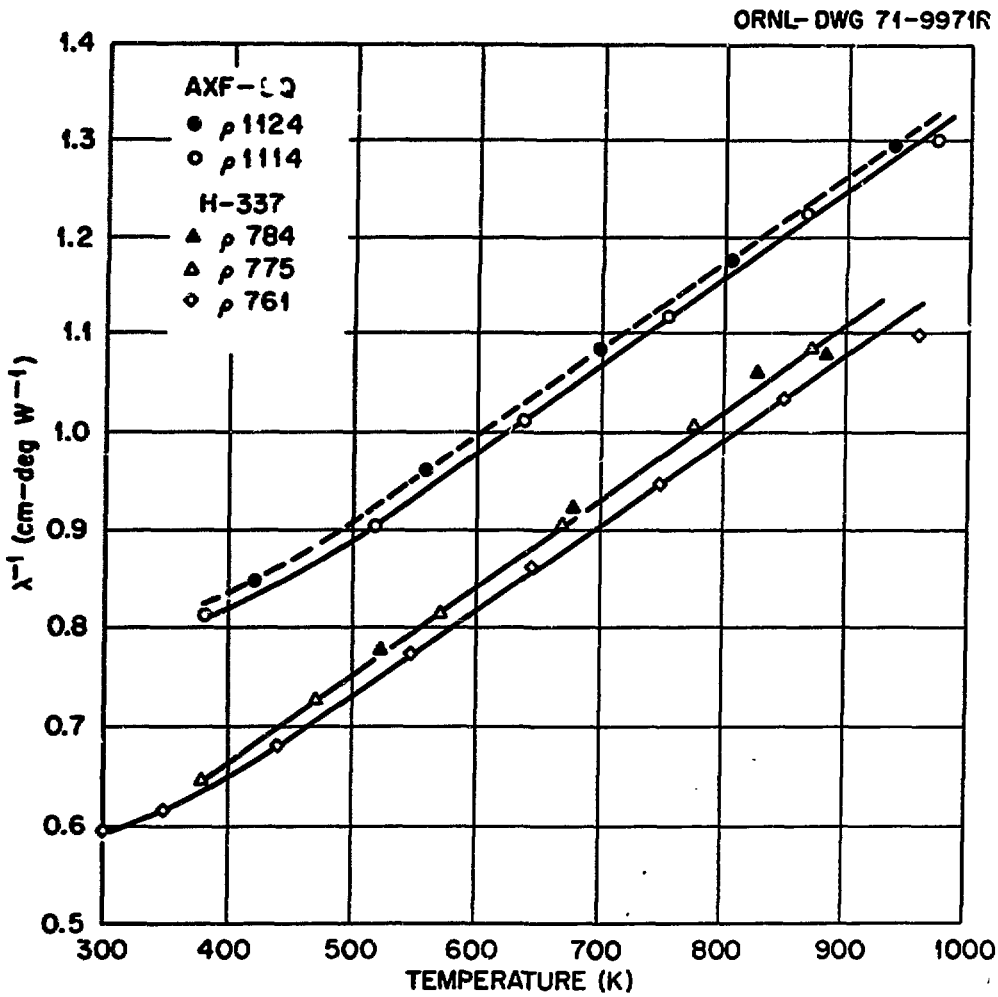
Fig. 3. Comparison of electrical resistivities of unirradiated and irradiated graphite vs temperature.

Fig. 4. Absolute Seebeck coefficients of unirradiated and irradiated AXF-5Q and H-337 graphite. For irradiated specimens the numbers in parentheses are Kelvin irradiation temperatures.

Fig. 5. Thermal conductivity vs temperature of unirradiated H-337 and AXF-5Q graphites and λ results from four irradiated specimens.

Fig. 6. Thermal conductivity of H-337 and AXF-5Q graphite vs neutron fluence from the present study and of other graphites from previous investigations. All data shown are for 300 K.

Fig. 7. The product of λ and ρ at 300 K vs fluence from Matsuo (1972) and from the present results.



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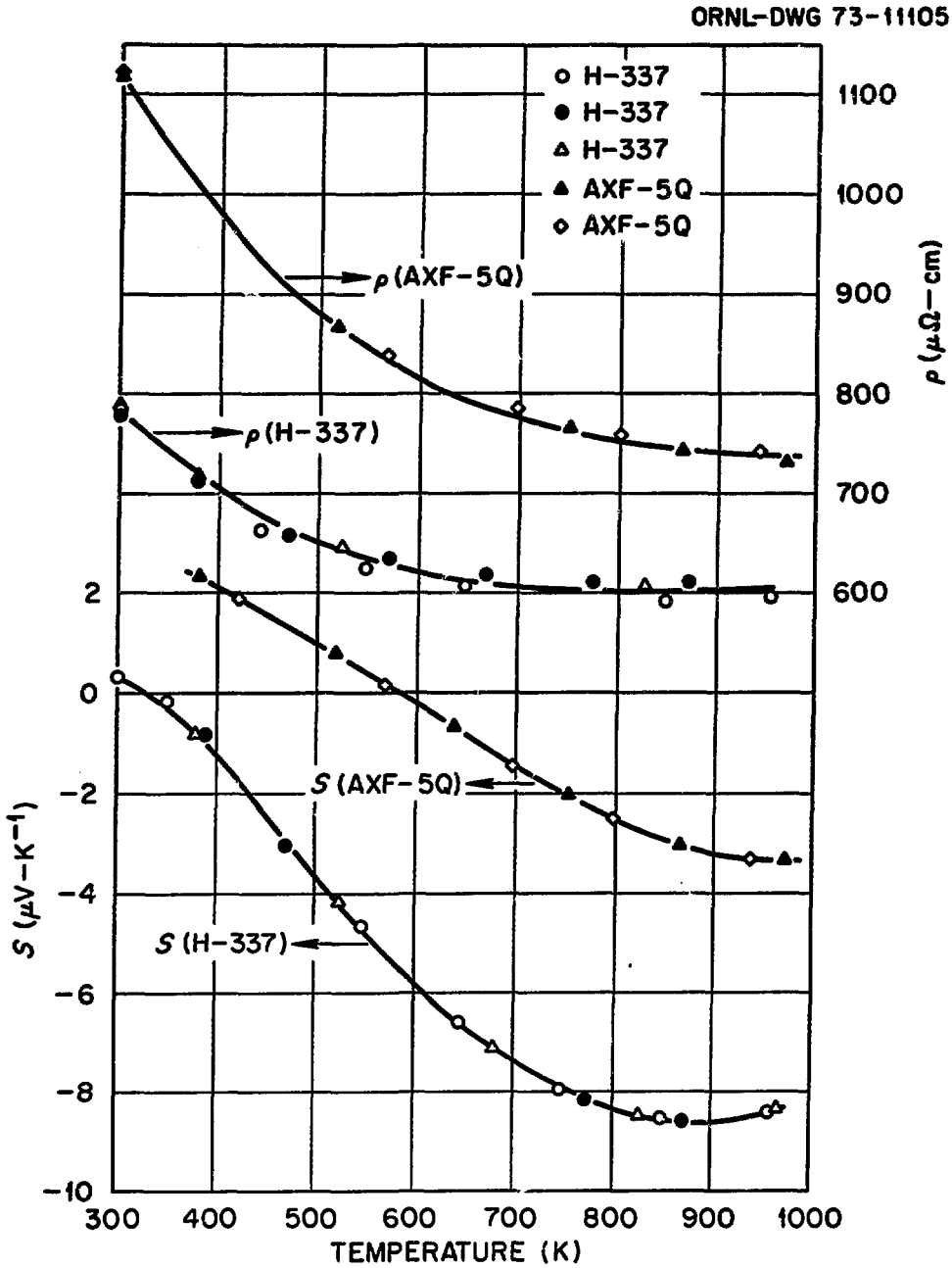

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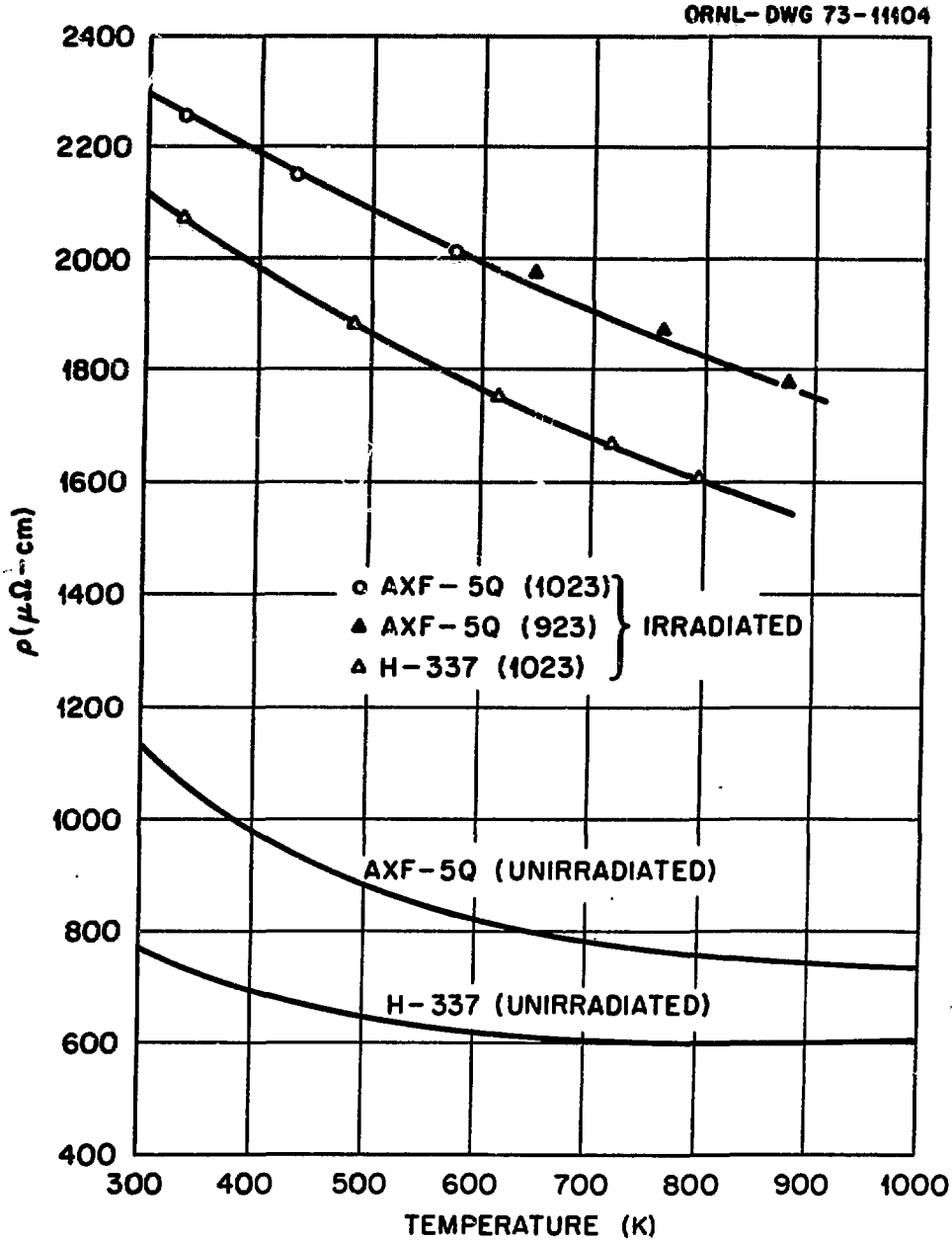

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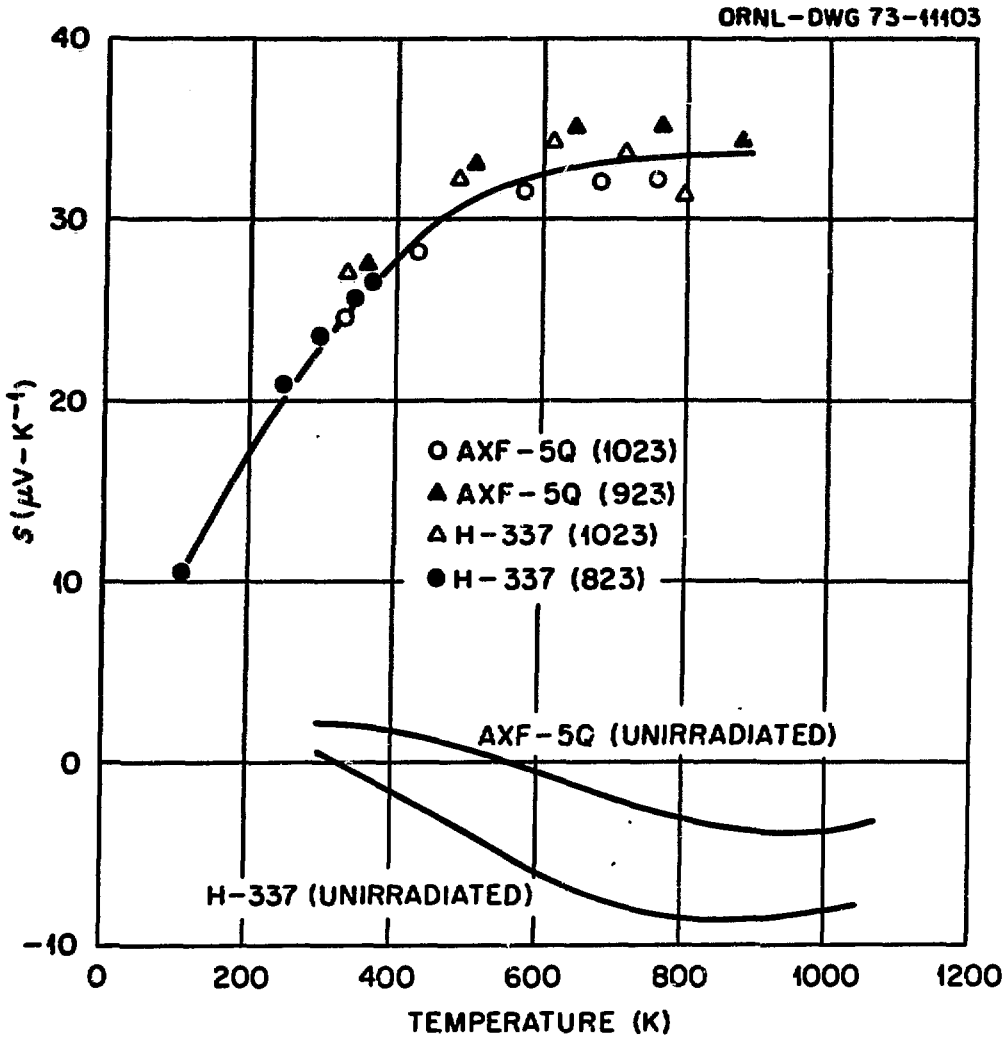

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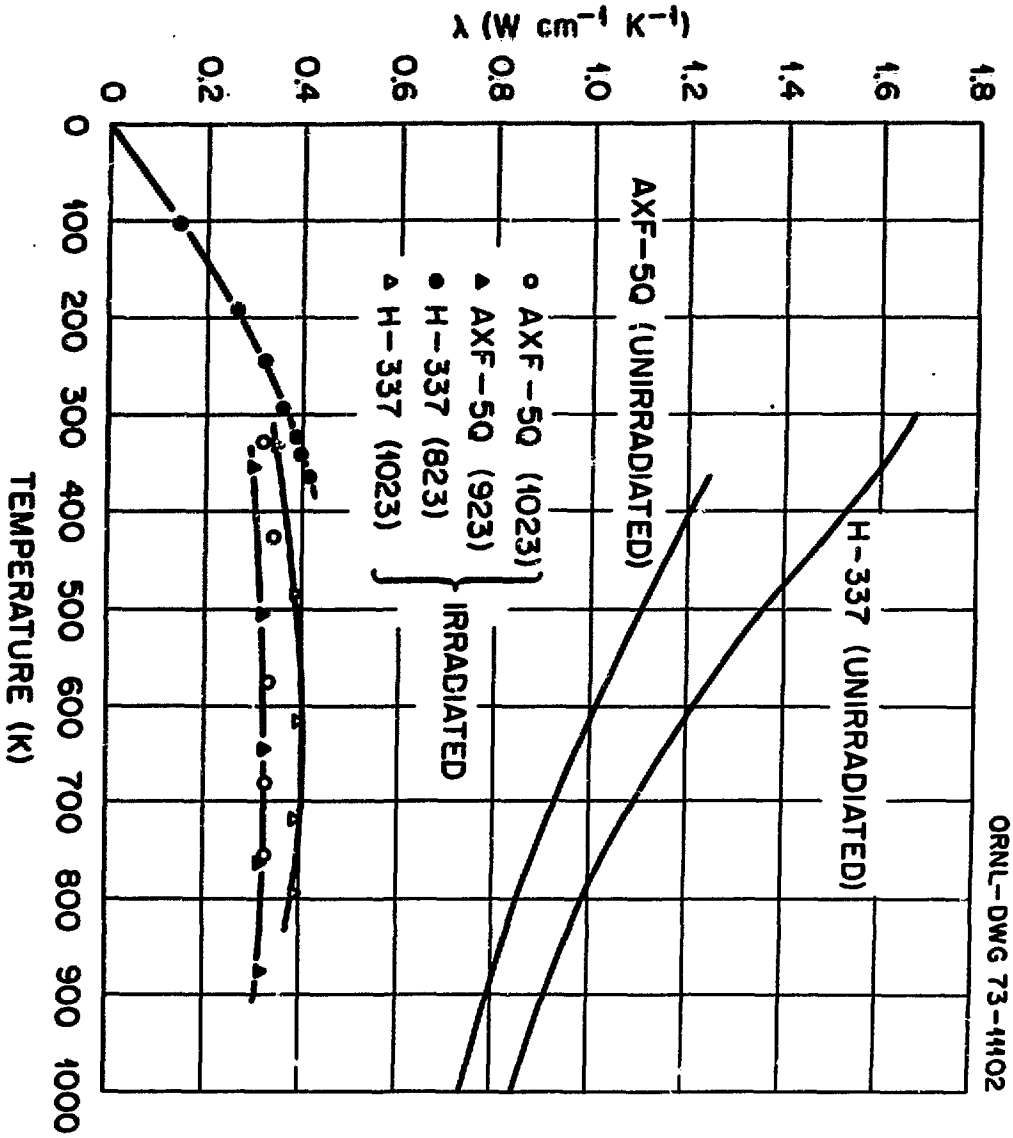

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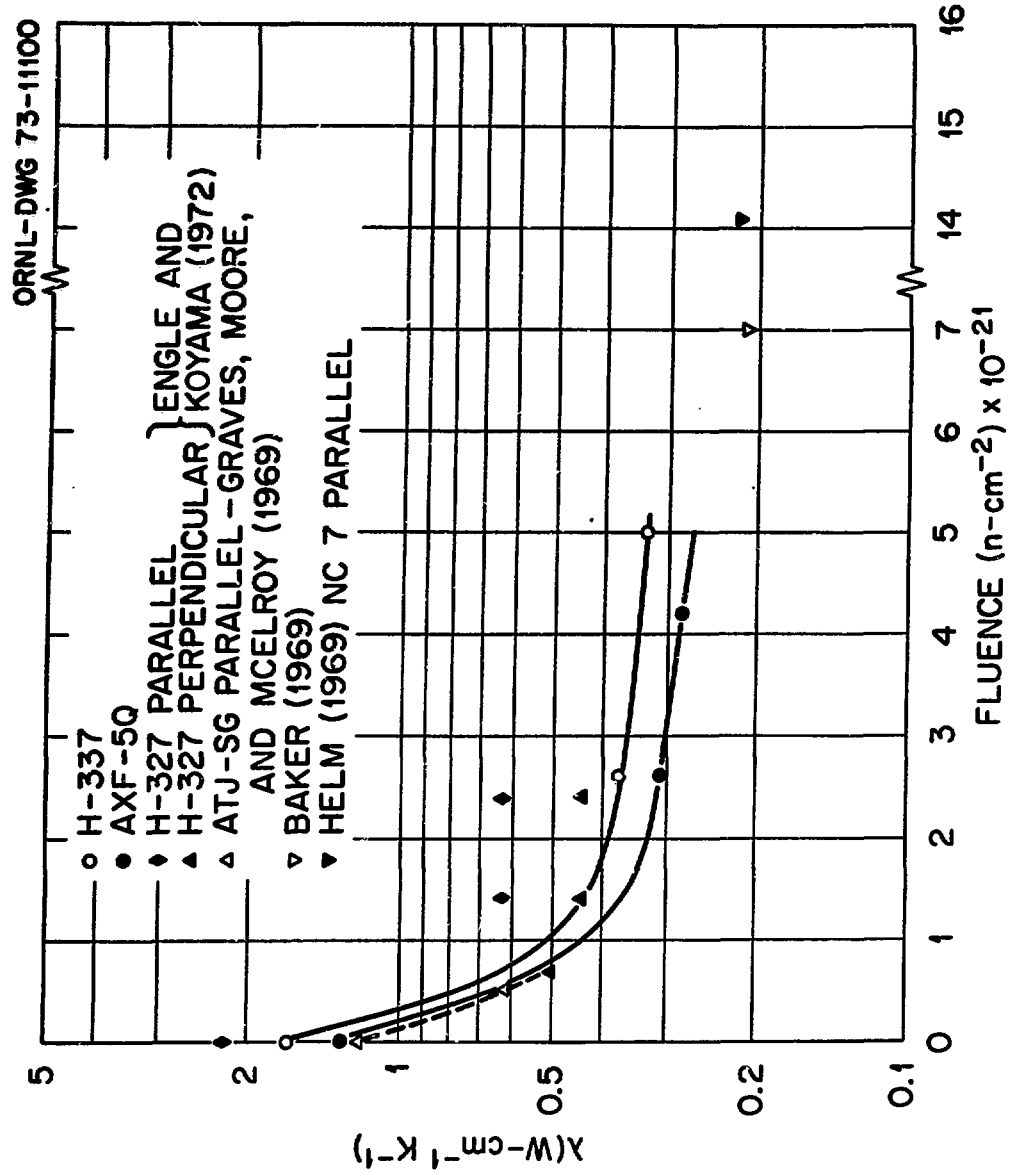

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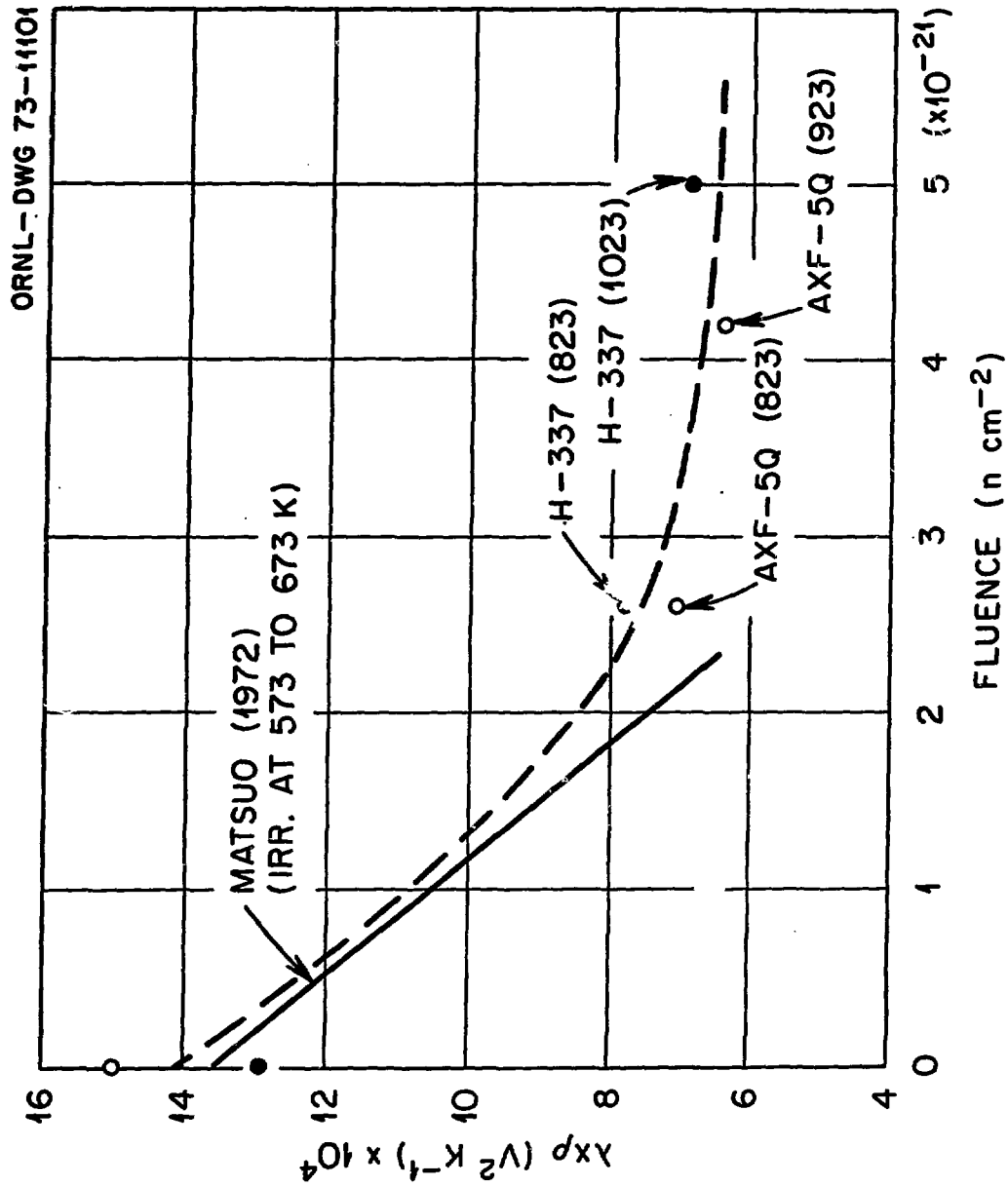

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