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by

W. A. Sibley and E. Sonder

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THE HARDENING OF KCl BY ELECTRON- AND GAMMA-IRRADIATION

W. A. Sibley and E. Sonder
Solid State Division, Oak Ridge National Laboratory*
Oak Ridge, Tennessee, U.S.A.

ABSTRACT

Measurements of the flow stress and F-band coloration have been made at room temperature on a number of different samples of KCl as a function of gamma- and electron-irradiation. The rate of increase of flow stress with irradiation is found to be greater (or smaller) in those samples and for those irradiation conditions for which the coloring rate is greater (or smaller). Moreover, the flow stress increase in any set of samples is proportional to the square root of the F-band absorption. The implication is that hardening is caused either by F-centers or other defects whose production is related to the production of F-centers. Since bleaching of F-centers does not produce any softening, and since the magnitude of the hardening is of the order of magnitude to be expected for interstitial type defects, the conclusion is drawn that the increase of flow stress due to irradiation of KCl is caused by interstitial Cl atoms or interstitial clusters.

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INTRODUCTION

It is now generally agreed that lattice hardening, the case in which the stress for the propagation of slip is increased by an increase in the stress required to move dislocations through the crystal, is a major contributor to the process of radiation hardening in alkali halide crystals. Recently, interest has centered on the problem of what defect or defects are effective in causing lattice hardening in irradiated crystals. Whapham and Makin[1] find that the hardening in LiF saturates at some constant value for large doses of electrons, and they have suggested that the lattice hardening is due to defect clusters or barriers. On the other hand, Nadeau[2] has suggested that the gamma irradiation hardening in LiF is produced by an interstitial type defect whose production may be related to the creation of F-centers.

Recent studies have shown that the coloring of KCl is a strong function of ionizing intensity[3] and varies greatly in different crystal ingots.[4,5] Moreover, evidence that hardening may depend upon radiation intensity has been obtained recently by Akimoto and Sibley[6] who observed that the behavior of the flow stress increase depended upon whether the crystal was irradiated with gamma-rays or with electrons. They predicted that this different behavior was most likely due to the difference in irradiation intensity of the two irradiation sources. These observations indicate that a careful study of the correlation between color center formation and hardening as a function of radiation intensity in KCl may be a fruitful approach to the problem of establishing the mechanism of hardening in these crystals.

EXPERIMENTAL PROCEDURE

Deformation samples of 0.7-1.0 cm length and about 0.05-0.10 cm^2 cross-section were prepared by cleaving from large ingots of single crystals obtained from the Harshaw Chemical Company, Isomet Corporation, and Optovac Corporation. Only those specimens which had no observable cleavage steps or grain boundaries were utilized. After cleavage the samples were wrapped individually in 1 mil aluminum foil for the irradiations. Experimental details for the preparation of the optical plates, which were cleaved from sections of the ingot adjacent to the deformation samples, have been described previously.[4,7]

The irradiations were performed using a Van de Graaff electron accelerator producing 1.5 Mev electrons and a Co^{60} gamma source of 4.1×10^6 r/hr. The electron current densities at the samples were either 0.02 or 0.36 $\mu amp/cm^2$. The temperature of the samples during the irradiations, as measured by a thermocouple which was inserted between two optical plates of KCl which were within the sample holder used, never exceeded 35°C. Optical measurements were made with a Gary model 14R spectrophotometer and an Instron testing machine operating with a crosshead speed of 0.05 cm/min was used to obtain the flow stress.

Since it is well known that small amounts of optical bleaching can increase the concentration of M, N, R, and other electron excess aggregate centers, it was felt necessary to check whether total darkness would have to be maintained during the deformation measurements. A group of samples was gamma-irradiated for two hours and then measured, some without having been exposed to light and the others after various amounts of optical bleaching. The results, shown in Fig. 1, indicate that although small changes do seem to take place during bleaching they are not much greater than the random variations observed between samples. This result is in agreement with the observations of Podachewski[8] that optical bleaching of X-irradiated NaCl caused no change in the flow stress. Consequently, the technique adopted for the measurements was to keep the samples in the dark during the irradiations by wrapping them in aluminum foil, but to determine the stress-strain curves in subdued light. The arrow shown in Fig. 1 gives an estimate of the amount of bleaching the samples undergo between the time they are unwrapped and the time the flow point is reached.

In view of the fact that the colorability of KCl varies widely from crystal to crystal,[4] and can vary by as much as 20% for crystals cleaved from the same ingot,[5] care was taken to eliminate large variations that might arise from differences between samples. In determining the average flow stress for any given irradiation, a minimum of six samples was used. Also, all specimens, both optical and deformation, used for a particular experiment were cleaved from the same portion of one crystal ingot wherever this was possible.

EXPERIMENTAL RESULTS

A. Dependence of the Flow Stress on Sample Preparation

As mentioned above, the F-center coloration rate of different KCl crystals varies widely presumably because of differences in growth techniques. This same variation is observed in the rate of increase of the flow stress as is shown in Fig. 2, where data for crystals obtained from the three commercial sources mentioned earlier are reproduced. The upper portion depicts the absorption coefficient of the maximum of the

F-band, corrected for the M-center absorption under the F-band[4] as a function of gamma ray dose; the lower portion shows the corresponding increase in the flow stress. The similarity between the coloring and the hardening in the four crystals is quite evident, particularly when it is remembered that theoretically one would expect the flow stress to increase as the square root of the concentration of barriers or effective defects in the lattice.[1]

In order to demonstrate the quadratic relation quantitatively, the incremental flow stress, $\Delta\tau = \tau(\text{irradiated}) - \tau_o$, is plotted logarithmically versus the height of the F-band in Fig. 3. The dotted line of slope one-half drawn through the points fits quite well for most of the points. However, for those points obtained after the shortest irradiations, significant deviations are evident, especially in the case of the Optovac and Isomet samples. The magnitude and direction of the deviations are such as would be obtained if a small fraction of F centers introduced during the early stages of irradiation was not accompanied by hardening (note that on this type of plot, the portion of the curve that on a linear graph would be near the origin is greatly expanded).

B. Dependence of the Flow Stress on Irradiation Intensity

Optical and deformation measurements were performed on a group of specimens from the same crystal ingot (H-50) after irradiation with 1.5 Mev electrons at two different current densities and after irradiation with Co^{60} gamma rays. The results are plotted as a function of energy absorbed in the samples in Fig. 4. The rate of energy absorption for the 3 samples is shown on the curves. The data for an absorption rate of 1.3 x 10^{11} Mev/cm^3 sec are the same as those for sample H-50 in Fig. 2.

When the results for the electron irradiations at different current densities are compared a correlation between coloring rate and increase in flow stress is apparent. For the two sets of samples irradiated with electrons, both the rate of coloration and of hardening were greater for the higher current density. However, when the comparison is made between electron- and gamma-irradiated specimens, the correlation is not so good. The coloring rate (has also been shown previously[4,7]) of the gamma-ray-irradiated samples is lower and consistent with the lower rate of energy absorption. But the hardening in the gamma-ray case seems to occur more rapidly or at least as fast as that for samples absorbing energy from the electron accelerator a factor of four faster.

DISCUSSION

A. Relationship between F-Centers and Hardening

As shown by Fig. 3, the increase in hardening is proportional to the square root of the F-center concentration for moderately heavy irradiation. The deviation from this relationship apparent at small doses of irradiation can be separated when the incremental increase in hardening is plotted linearly against the square root of the F-band absorption. Figure 5 is such a plot for one of the sets of samples, Isomet-100. It is clear that the curve does not pass through the origin originally, but can be made to do so by plotting $\Delta\tau$ versus $(\alpha_F' - \alpha_o)^{1/2}$, where α_o can be considered to be the absorption due to F centers which are not associated with an increase of flow stress. In the case of the sample in Fig. 5, $\alpha_o = 16$, a value that is of the same order of magnitude as the height of the first stage of F center coloration.[4] In a similar manner values for α_o were obtained for most of the samples used and are shown in Table I. A comparison of these values with estimates of the height of the first stage (column 4 of Table I) for the various samples reveals enough similarity to suggest that F centers introduced during the fast, first stage of coloration are not associated with an increase in the flow stress.

Even though all of the samples except one (the sample irradiated with an electron intensity of 0.36 μamp/cm^2 which will be discussed below) exhibited a square root dependence on the F center concentration, the ratio $d(\Delta\tau)/d(c^{1/2})$, where c is the mole fraction of F centers, varies somewhat between sets of samples.[9]

For irradiations at the highest current density of electrons, it was not possible to fit the data to a square root dependence of the F center concentration as discussed above. The logarithm of $\Delta\tau$ plotted vs the logarithm of $(\alpha_F' - \alpha_o)$ yields a slope of 0.6 rather than the 0.5 obtained for all of the other samples. Figure 6 shows the results for this set of samples as well as the combined results for the other sets. In the figure the five "normal" samples have been normalized to fall on the same line by dividing each set of data by its value $d(\Delta\tau)/d(c^{1/2})$; the scale for the sample with slope 0.6 has been shifted by a factor of 2.

There is a possible explanation for this anomalous observation. The irradiations for this particular set of samples were interrupted every two minutes to permit the samples to cool from about 33 to 35°C to room temperature (25°C). In the case of the other samples, measurements of temperature within a dummy sample indicated that uninterrupted irradiation would cause the temperature to equilibrate near 30-32°C for the low intensity electron irradiation (0.02 μamp/cm^2) and near 29°C in the gamma source. Also, since the optical specimens were irradiated in more massive holders than were the samples used for deformation, it is possible that the optical plates attained a somewhat higher temperature than the deformation specimens; this is particularly true for the high current density. Thommen[10] has observed that in the vicinity of room temperature the coloring behavior of KCl is very temperature sensitive. If the anomalous slope observed is due to temperature variation, then a careful investigation of irradiation hardening as a function of temperature might be very illuminating.

B. The Hardening Centers in KCl

Whapham and Makin[1] found that the hardening of LiF saturates and that irradiation with more than 3 x 10^{15} electrons/cm^2 (current densities used were equal to or less than 0.5 μamps/cm^2) caused no further increase in the flow stress. They attributed this saturation to a clustering of defects into lattice barriers. In the case of the present experiments on KCl, complete saturation was not attained. Figure 7 depicts the data, which are also shown in Fig. 3, for the highest current density of the electron irradiation plotted versus the square root of the number of electrons impinging on the samples. This figure permits a direct comparison with the work of Whapham and Makin; it is clear that even though curvature is present in Fig. 7 no complete saturation occurs for electron doses up to 5 x 10^{15} electrons/cm^2. The curvature seems to be of the same magnitude as the curvature observed in F center introduction curves for these and similar samples,[7] indicating that at least qualitatively the hardening in KCl is related to the F center concentration even at very high doses.

The fundamental damage process in the alkali halides is one of ionization rather than ion displacement.[11] This idea is illustrated very clearly by the intensity dependence of both the F center production and the increase in the flow stress. However, Whapham and Makin did not find an intensity dependence of the flow stress in their electron irradiation of LiF crystals. It would be interesting, therefore, to know if there is an intensity dependence of the coloring in LiF since it is known that in some ways LiF does not act like the other alkali halides in its coloration properties.[12]

The square root relation between the hardening and the F center concentration is to be expected if the F centers are the entities causing resistance to dislocation motion. However, as shown in Fig. 1 very little change in the flow stress occurs when crystals having an F band absorption of $\alpha_F' = 20\ cm^{-1}$ are bleached with white light until $\alpha_F' = 1\ cm^{-1}$. Further, a comparison of the flow stress for additively colored KCl crystals, as found by Suzuki and Doyama,[13] with that of irradiated crystals containing about the same F center concentration indicates that it is not the F center itself which contributes to the hardening.

When crystals containing a large concentration of F centers are optically bleached other centers are formed which are now generally believed to be aggregate centers composed of two or more F centers.[14] These centers can also be eliminated as major contributors to the hardening since on optical bleaching their concentrations increase by over a factor of 100, whereas no corresponding increase in the flow stress is observed.

Fleischer[15] has predicted that the increase in stress at $0^{\circ}K$

due to defects producing elastic lattice distortions is given by:

$$\Delta\tau = (G/n)\ c^{1/2} \qquad (1)$$

where G is the shear modulus, c is the mole fraction of defects, and n is related to the tetragonal lattice strain associated with the defect. n is a number which can vary between 100 for divacancies and 3-10 for defects producing large tetragonal lattice strain such as interstitials or interstitial clusters. Since G for KCl is about 1×10^9 dynes/mm^2, the ratios given in Table I, column 5, yield values for n around 7. According to Fleischer such a value would be characteristic of interstitials or interstitial clusters. It is not possible to decide between the two possibilities. However, if interstitial clusters are responsible for the increased hardening, then they must form even for low irradiation doses and their diameter would be ~ 30 Å.

SUMMARY

1. The increase of flow stress under irradiation depends on the origin of the crystals in the same way as does the F-band coloration.

2. The increase of flow stress produced by a given amount of absorbed energy depends upon the rate of energy absorption. It is greater for greater absorption rates.

3. The increase in flow stress is proportional to the square root of the F center concentration for KCl.

4. Optical bleaching experiments eliminated F, M, R, and N centers as dominant hardening centers in irradiated KCl.

5. No saturation of the flow stress with irradiation dose was observed for irradiation doses up to 6 times that necessary to produce

2×10^{18} F centers/cm^3. (Optical measurements of the F center concentration in 0.2 mm thick crystals could be made only to a concentration of 2×10^{18} centers/cm^3.)

6. The experimental results agree with the theoretical calculations of Fleischer for hardening caused by either interstitial halogens or interstitial clusters.

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Table I. Parameters Obtained from Analysis of Data

1 Sample	2 Irradiation[a]	3 α_o (cm^{-1})	4 α_F (first stage) (cm^{-1})	5 $d\Delta\tau/d(c^{1/2})$[b] (kg/mm^2)
H 40	γ	4	~ 5	160
H 50	γ	3	~ 7	140
H 50	e (.02 $\mu A/cm^2$)	7	~10	110
I 100	γ	16	~10	160
O 100	γ	14	~17	170
H 50	e (.35 $\mu A/cm^2$)	15	~15	~140

a -- γ indicates Co^{60} gamma irradiation.

e indicates 1.5 Mev electron irradiation at current density given.

b -- $d\Delta\tau/d(c^{1/2})$ is proportional to the slope of curves similar to Fig. 5. See also footnote No. 9.

FIGURE CAPTIONS

Fig. 1 The Effect of Bleaching on the Flow Stress of a KCl Sample Gamma-Irradiated for Two Hours. For the initial point the samples were in total darkness both during irradiation and measurement. Bleaching was done with a 100 watt incandescent light 1 foot away from the samples. The arrow is drawn to indicate the bleaching to be expected in samples whose stress strain curves are obtained in subdued room light.

Fig. 2 The Increase in Flow Stress and F center Coloration Produced by Irradiating Different Sets of Samples of KCl in a 4.1 million r/hr Co^{60} Gamma Ray Source. Crystals H-40 and H-50 were purchased from Harshaw; I-100 and O-100 were purchased from Isomet and Optovac respectively.

Fig. 3 The Relation between Hardening of KCl and the Increase of F-Band Absorption. Log change in yield stress is plotted versus log α_F'. Symbols are the same as in Fig. 2.

Fig. 4 The Effect of Radiation Intensity on Hardening and F-center Production. Samples used were all from ingot H-50. The full circles indicate electron irradiation at a current density of 0.36 $\mu A/cm^2$. The diamonds are for data obtained at electron current density of 0.02 $\mu A/cm^2$. The triangles are for gamma irradiation.

Fig. 5 Increase in Flow Stress vs $(\alpha_F')^{1/2}$. Open squares are the experimental data for Sample I-100. The black squares were obtained by subtracting a constant amount (α_o = 16) from the absorption coefficients.

Fig. 6 Composite Plot of Log Flow Stress versus Log ($\alpha_F' - \alpha_o$). The curves for all sets of samples except one have been normalized. The data obtained for high intensity electron bombardment, yielding a slope of 0.6 are discussed in the text.

Fig. 7 Increase in Flow Stress Plotted versus the Square Root of the Electron Dose. The scales are chosen to make possible direct comparison with LiF work (ref. 1).

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9. c has been calculated from the equation:

   $C = (1.1 \times 10^{16}/N_o)\ \alpha_F'\ \epsilon$. Where $N_o = 1.6 \times 10^{22}$, α_F' is the peak height of the F band absorption; ϵ is the half width of the F band at room temperature (0.35 ev).
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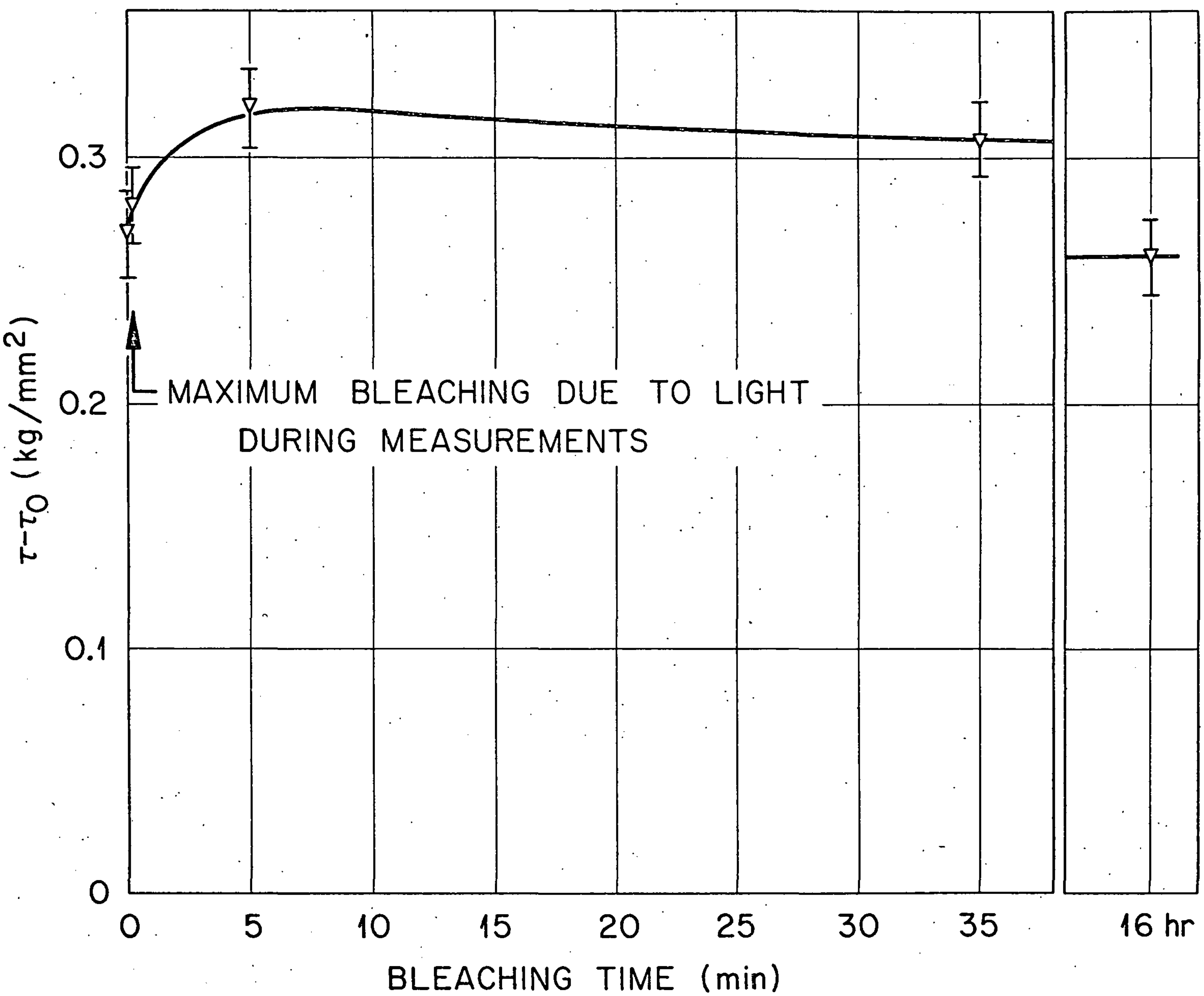


Fig. 1

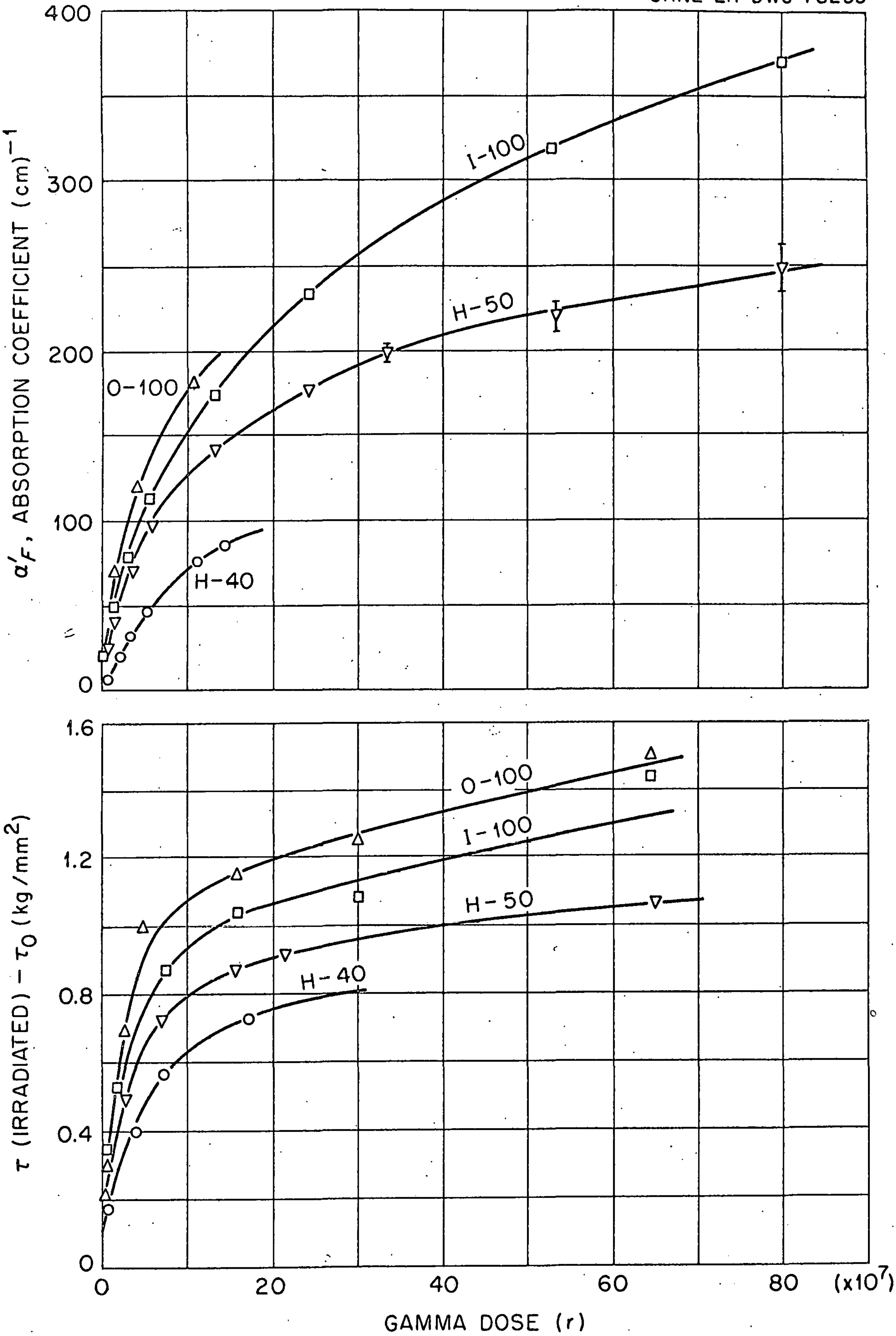
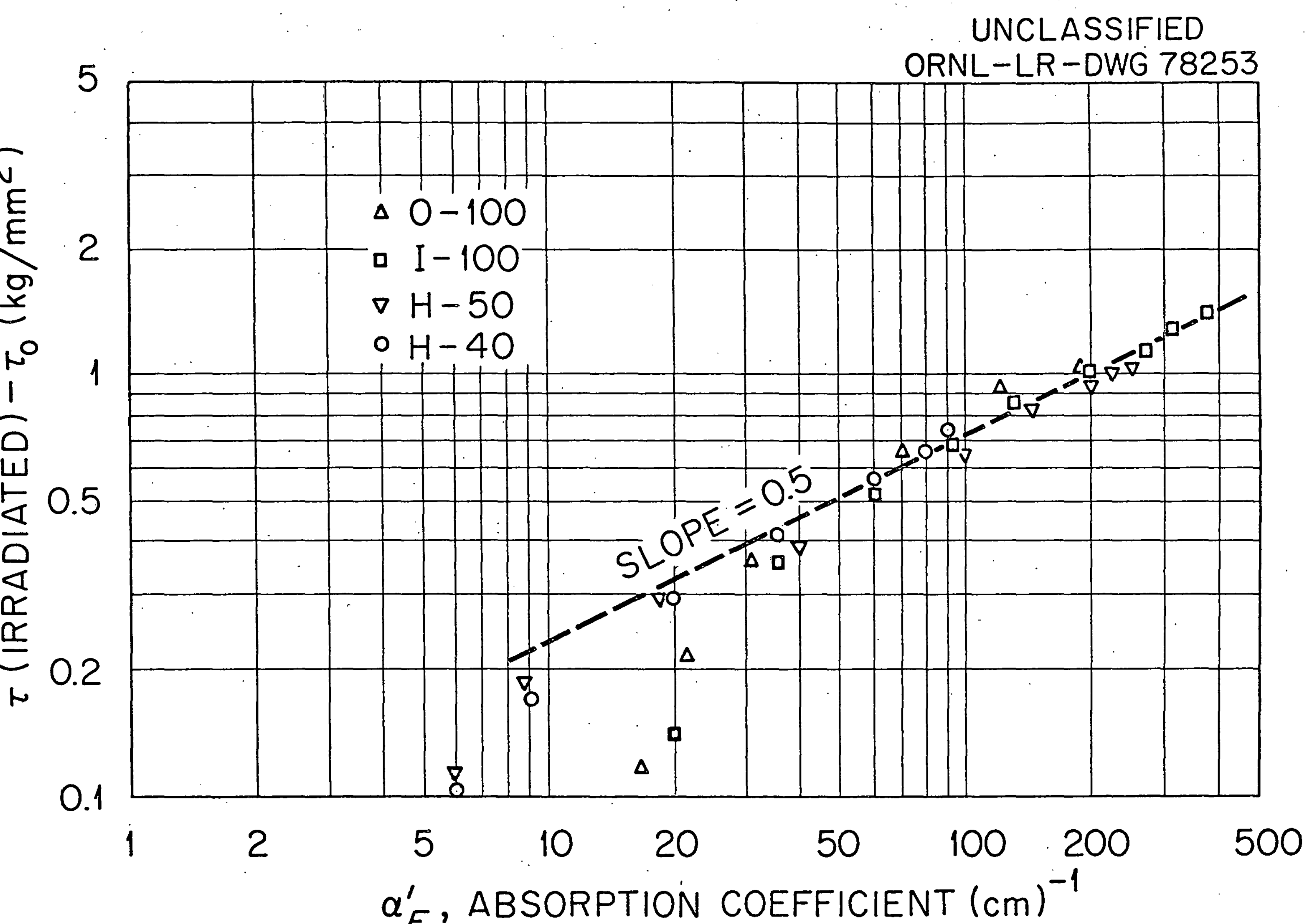

400
300
200
100
0
α'_F, ABSORPTION COEFFICIENT (cm)$^{-1}$
I-100
H-50
O-100
H-40
1.6
1.2
0.8
0.4
0
τ (IRRADIATED) $- \tau_0$ (kg/mm^2)
O-100
I-100
H-50
H-40
0
20
40
60
80
(x10^7)
GAMMA DOSE (r)

Fig. 2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O-100
I-100
H-50
H-40
SLOPE = 0.5
τ (IRRADIATED) − τ0 (kg/mm2)
α'F, ABSORPTION COEFFICIENT (cm)−1
5
2
1
0.5
0.2
0.1
1
2
5
10
20
50
100
200
500

Fig. 3

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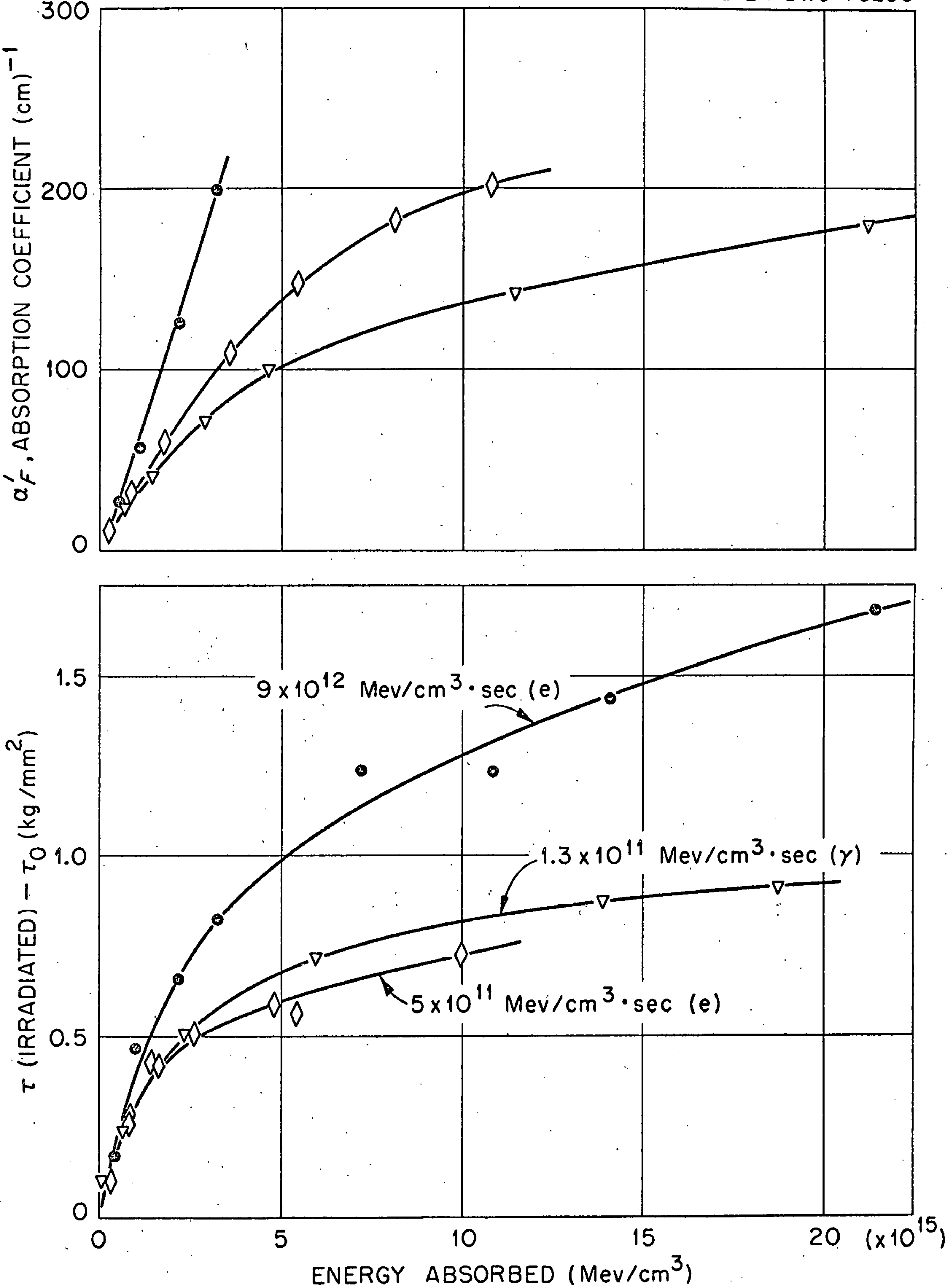

Fig. 4

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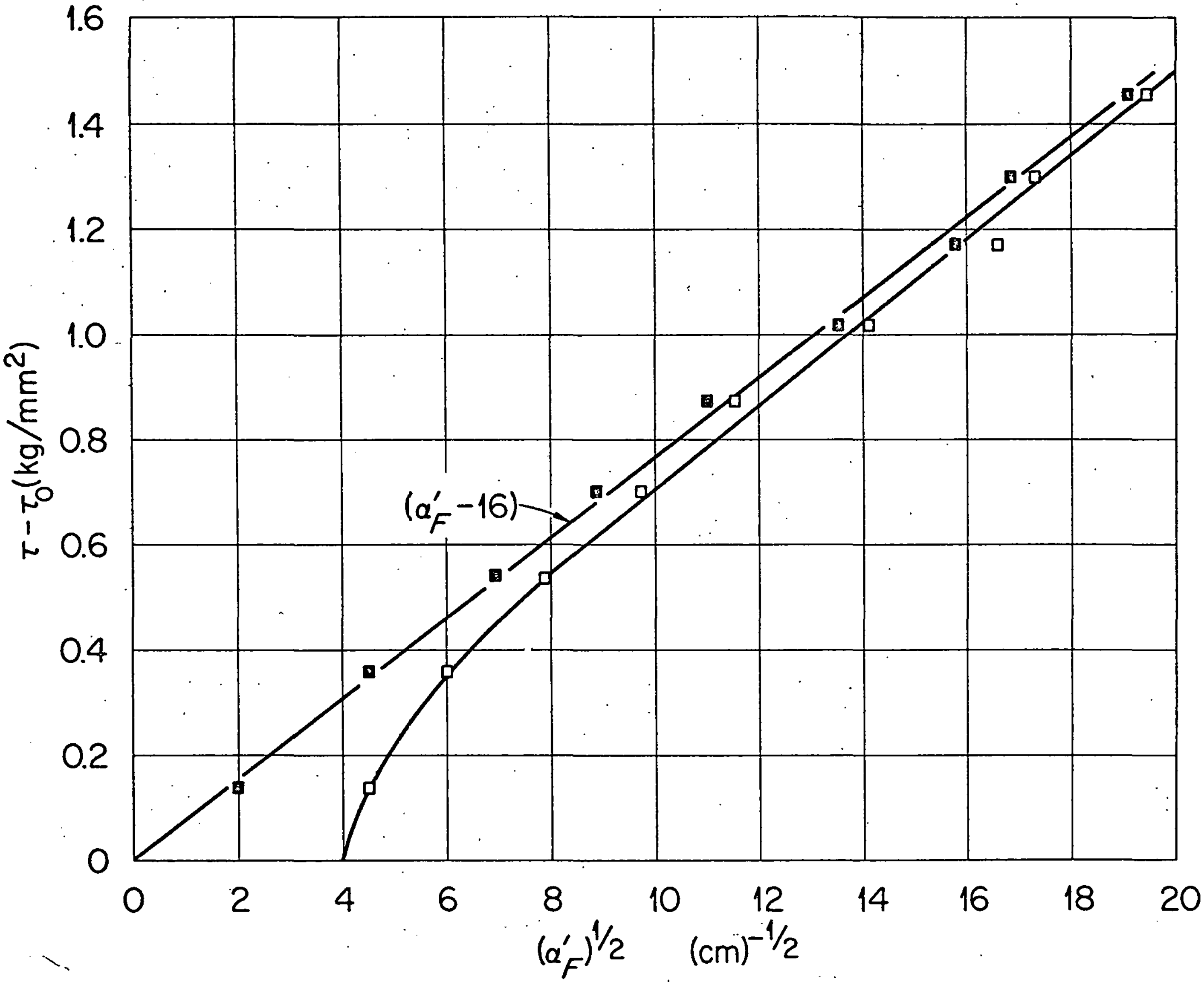

Fig. 5

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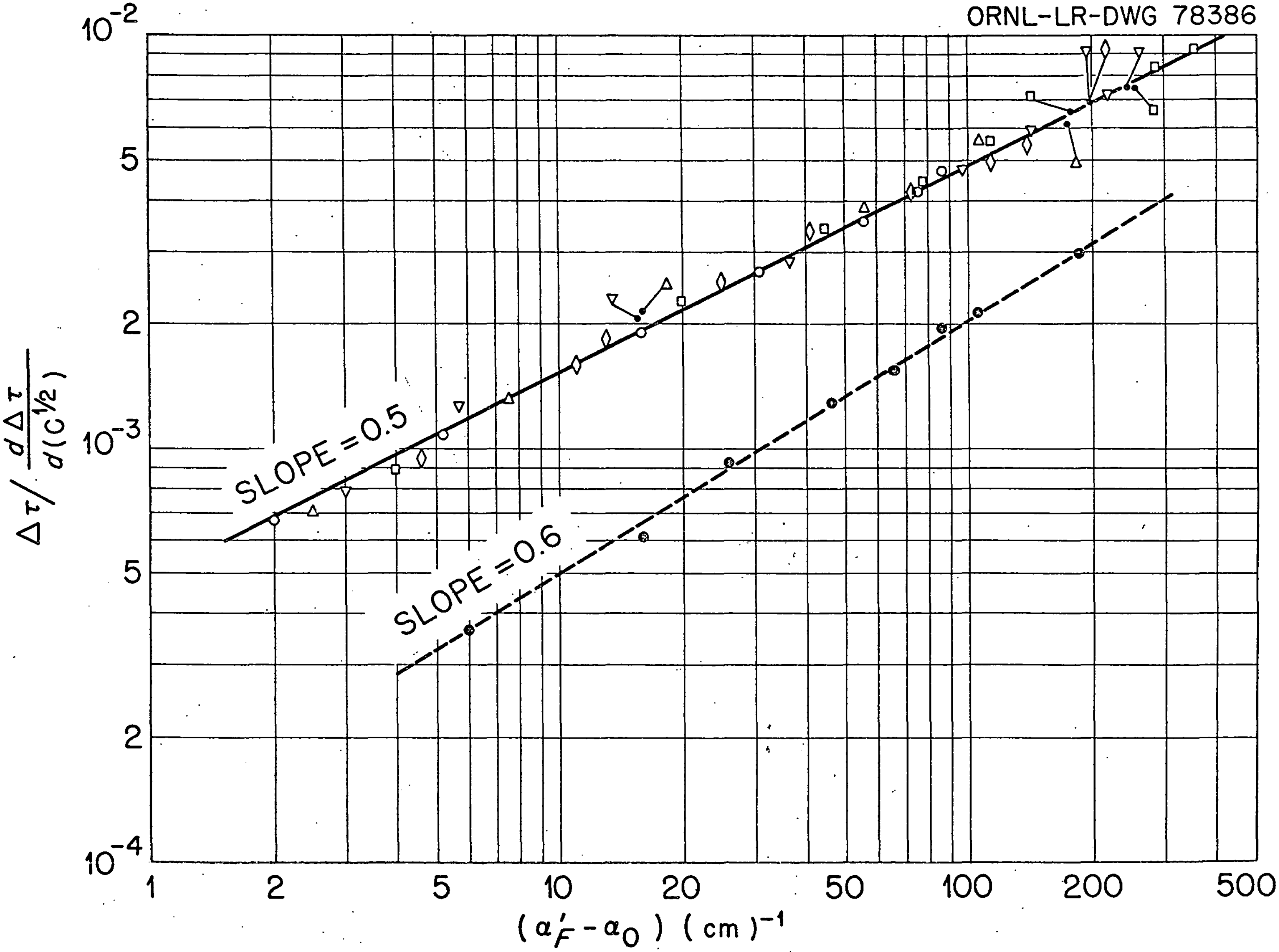

Fig. 6

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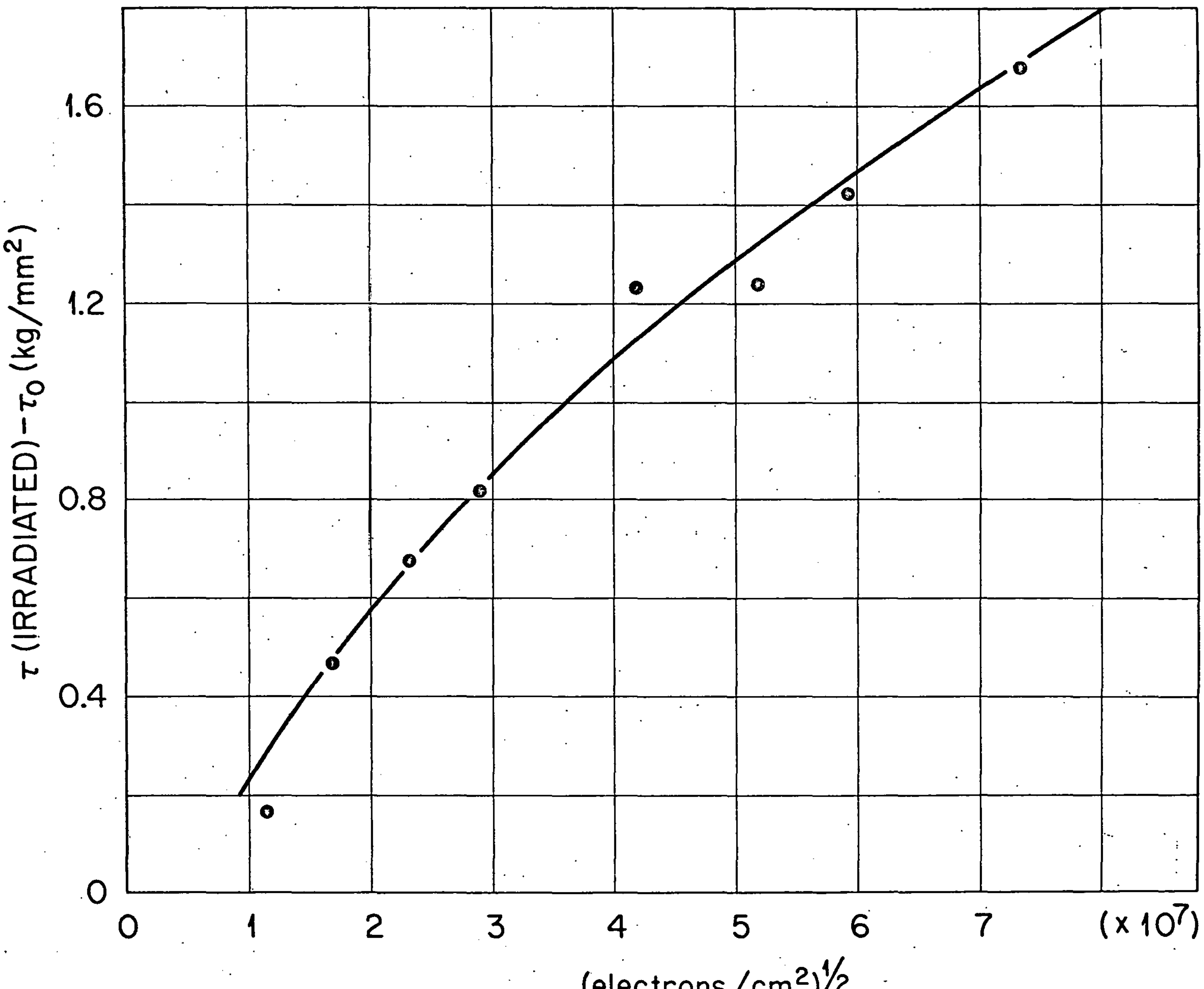

Fig. 7