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Dependence of the Optical Bleaching Rate of X-Irradiated KCl Crystals on Light Intensity

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Measurements have been made on the changes in the bleaching rate of the *F* band as the result of varying the intensity of *F* light. Bleaching was done on KCl crystals which had been irradiated at room temperature with hard x rays into either the first or second stage of coloration. In the first stage irradiated crystals the total bleaching of the *F* centers during the first ten seconds of illumination varied approximately linearly with light intensity at low intensities, but becomes saturated at intensities greater than 5×10^{14} photons/sec cm^2. The bleaching process is thought to occur primarily through the capture of photoelectrons at pre-existing electron traps. Based on this model it is possible to set up the kinetic equations for the bleaching process. Using reasonable values for photoelectron capture coefficients forces one to conclude that the number of photoelectrons is always very small throughout the bleaching process. The resulting simplification in the analysis of the kinetic equations leads to a prediction of the experimentally observed variation of the initial bleaching rate with light intensity. The analysis shows that the ratio of the capture coefficient for photoelectrons of the electron trapping centers to that of negative-ion vacancies is about unity, which strongly suggests that the trapping centers are either traps with net positive charge or are neutral traps located close to the original *F* centers.

The rate of bleaching during the second stage of bleaching saturated at the lowest intensity used which was about 1×10^{14} photons/sec cm^2. This result is discussed in terms of the analysis given for the first stage of bleaching.

INTRODUCTION

A SERIES of experiments on the optical bleaching of x-ray irradiated KCl samples have been performed in this laboratory. A recent paper[1] has dealt with the kinetics of bleaching of *F* centers with *F* light in the temperature range of -30°C to $+10$°C. It was shown in this paper that the bleaching of *F* centers can be described as a superposition of two processes, a rapidly decaying, temperature independent process plus a temperature dependent process. The temperature dependent process is probably controlled by a diffusion process which has an activation energy in the vicinity of 0.35 ev. In contrast, the temperature independent process is considered to occur through the transfer of electrons from *F* centers to some fixed number of unidentified electron trapping centers which exist in the crystal prior to bleaching. The present paper is concerned primarily with the latter, temperature independent process, and was designed to obtain information on the nature of the electron trapping centers.

In this relatively simple bleaching process, the photoelectrons created at *F* centers are either transferred to trapping centers or returned to negative-ion vacancies to reform *F* centers. One may anticipate the effect that varying the intensity of *F* light would have on the rate of bleaching of *F* centers. After illumination with low intensity *F* light for a fixed, small interval of time, one should expect that a fraction of the trapping centers are filled with electrons and that a corresponding number of *F* centers have been bleached. Small increases of light intensity would result in a proportional increase in the number of bleached *F* centers. There should exist, however, a light intensity for which all of the electron trapping centers become occupied in the fixed time interval. Increasing the light intensity above this value would then serve only to increase the number of photoelectrons present during the illumination, but would not result in an increase in the number of bleached *F* centers.

In this experiment we have observed the changes in the initial bleaching rates of *F* centers during illumination with various intensities of *F* light. It will be shown that the results are amenable to an analytical interpretation which yields information on the capture coefficient of the electron trapping centers. Although the analytical treatment is confined in this paper to the results of the present experiment, the treatment can easily be applied to a number of similar cases.

EXPERIMENTAL METHOD

Samples approximately 10×10×1 mm in size were cleaved from a large single crystal of KCl obtained from the Harshaw Chemical Company. All samples were colored by subjecting them to x-rays from a copper target operated at 40 kv and 20 ma. The x-ray unit contained voltage and current regulating circuits. X-rays were filtered through 1.5-mm thick crystals of NaCl, so as to filter out the soft component. During the irradiation the sample was mounted at a distance of 3 inches from the x-ray port with the large face perpendicular to the x-ray beam. The irradiation was performed under ambient conditions in the dark.

Optical absorption measurements were made in a Beckman Model DU, spectrophotometer equipped with a stabilized ac power supply. Optical bleaching was accomplished in the spectrophotometer with the slit set at 2 mm, and the wavelength set at 560 mμ (*F* light). Under the conditions the spectral band width of the bleaching light was approximately 100 mμ. Rough light intensity measurements were made with a Photovolt Model 200 photometer which had a special selenium photocell as the sensing unit. The calibration supplied by the manufacturer was applied to the measurements.

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[1] W. E. Bron and A. S. Nowick, Phys. Rev. **119**, 114 (1960).

A range of bleaching light intensities of 1×10^{14} to 7.4×10^{14} photons/sec cm^2 was obtained by placing between the monochromator and the crystal a series of Kodak neutral density filters.

It was necessary to compare the bleaching rate of the F band for various light intensities in a number of samples which had the same initial F band absorption. Because of fluctuations in the room temperature and in the characteristics of the x-ray tube during irradiation, it was only possible to obtain samples whose initial F band absorption coefficient (α_{F0}) varied by $\pm5\%$ about some desired mean value. It has, however, been observed in a series of experiments that the bleaching curves of a number of such samples differing slightly in α_{F0} can be superimposed by a shift along the absorption scale. The bleaching curves were determined for a number of samples whose α_{F0} varied by no more than $\pm5\%$ and which were illuminated with light of the maximum intensity (7.4×10^{14} photons/sec cm^2). It was then possible to interpolate, point for point, the bleaching curves for these samples and obtain, to a high degree of accuracy, the corresponding bleaching curves for any desired α_{F0}. The bleaching curve obtained during illumination with light of less than maximum intensity was then compared with that obtained from maximum intensity light, with the two curves starting at the same α_{F0}.

The experiment was performed for a set of samples irradiated to near the end of the first stage of coloration[2] (mean $\alpha_{F0}=0.45$ mm^{-1}) and for a set irradiated into the second stage of coloration[2] (mean $\alpha_{F0}=0.60$ mm^{-1}).

EXPERIMENTAL RESULTS AND DISCUSSION

The effect of various F light intensities on the initial bleaching rate of the F band is plotted in Fig. 1. The ordinate of Fig. 1 gives the ratio of the change in the F band absorption ($\Delta\alpha_F$) in the first 10 seconds of bleaching under F light of a given intensity I to that under maximum intensity I^0. This quantity is plotted against the ratio I/I^0. It will be observed that for the crystal irradiated into the first stage of coloration ($\alpha_{F0}=0.45$ mm^{-1}) the rate of bleaching increases approximately linearly with intensity up to roughly 50% of the maximum intensity. Above this intensity, however, the rate of increase of the bleaching rate with intensity decreases sharply, i.e., the bleaching rate approaches some saturation value. In the crystals irradiated into the second stage of coloration ($\alpha_{F0}=0.60$ mm^{-1}) however, a deviation from proportionality to light intensity is not observed until about 80% of the maximum intensity.

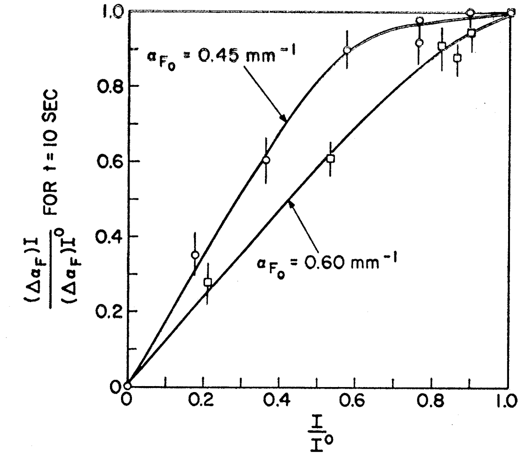

FIG. 1. Initial rate of bleaching as a function of the intensity of the light incident on samples irradiated into the first stage of coloration ($\alpha_{F0}=0.45$ mm^{-1}) and samples irradiated into the second stage of coloration ($\alpha_{F0}=0.6$ mm^{-1}). In this graph the ordinate is the ratio of the initial rate of bleaching of F centers with light of reduced intensity to the rate of bleaching using light of maximum intensity. The abscissa is the relative intensity of the incident F light.

The results shown in Fig. 1 support the bleaching process outlined in the introduction. It was proposed that bleaching occurs when photoelectrons are transferred to some unidentified electron trapping centers present in the crystal prior to bleaching. Alternatively, photoelectrons may return to negative-ion vacancies to reform F centers. It is possible to write the kinetic equations describing this bleaching process in the following way.[3]

$$dn_F/dt=-\sigma_F I n_F+k_v n_v n_e, \tag{1}$$

$$dn_T/dt=-k_T n_T n_e, \tag{2}$$

$$dn_v/dt=-k_v n_v n_e+\sigma_F I n_F, \tag{3}$$

$$dn_e/dt=-k_v n_v n_e-k_T n_T n_e+\sigma_F I n_F, \tag{4}$$

where n_F, n_T, n_v, n_e are the numbers/cm^3 of F centers, electron trapping centers, negative-ion vacancies, and photoelectrons respectively. I is the intensity of the bleaching light, σ_F is the capture cross section of F centers for photons, and k_v and k_T are the capture coefficients for photoelectrons of negative-ion vacancies and the electron trapping centers, respectively. The quantum efficiency for the optical ionization of F centers is taken to be unity.[4]

Two further relationships can be obtained from the requirement that negative-ion vacancies are created during bleaching only when F centers are bleached, and from the assumption that only F centers are sources of photoelectrons and that the only sinks are the electron trapping centers. This may be expressed as follows:

$$n_v=n_{F0}-n_F, \tag{5}$$

$$n_e=(n_{F0}-n_F)-(n_{T0}-n_T), \tag{6}$$

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[2] See W. E. Bron, preceding paper [Phys. Rev. **119**, 1853 (1960)].

[3] These equations are similar to those proposed by Hesketh. The conditions on the equations are, however, less restrictive so that the solution of the present equations is somewhat more general. R. V. Hesketh, thesis, University of Durham, Durham, England, 1953 (unpublished).

[4] H. Pick, Ann. Physik **31**, 365 (1938).

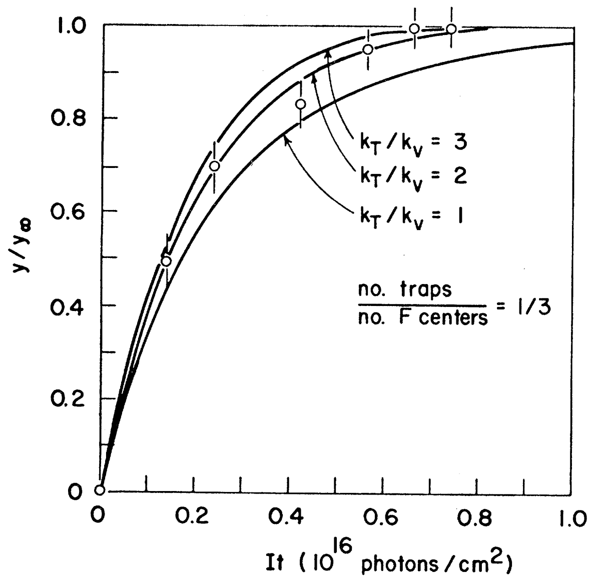

FIG. 2. Comparison of the experimental (open circles) and calculated (solid lines) variation of the number of bleached *F* centers as a function of the product of the light intensity (*I*) and the illumination time (*t*). The number of bleached *F* centers is given in terms of the parameters of Eq. (11). The ratio of the number of traps to original *F* centers is assumed to be $\frac{1}{3}$.

where n_{F0} and n_{T0} are the concentration of *F* centers and electron trapping centers just prior to bleaching.

If one makes the substitution that $y=(n_{F0}-n_F)/n_{F0}$ and $z=(n_{T0}-n_T)/n_{T0}$ and eliminates all variables but y and z, Eqs. (1) and (2) become:

$$\dot{y}=\sigma_F I(1-y)-n_{F0}k_v[y-(n_{T0}/n_{F0})z], \tag{7}$$

$$\dot{z}=n_{F0}k_T(1-z)[y-(n_{T0}/n_{F0})z]. \tag{8}$$

In order to solve Eqs. (7) and (8) for y and z it is necessary to make one further simplification. It is possible to obtain rough estimates of the magnitudes of some of the parameters involved in these equations. This is most easily shown in terms of the parameters of Eq. (4), i.e., $\sigma_F I$, $k_v n_v$ and $k_T n_T$. From the ratio of the absorption coefficient at the maximum of the *F* band to the concentration of *F* centers as obtained from Smakula's equation[5] one obtains a rough value for $\sigma_F \approx 1.4\times 10^{15}$ cm^2. For the maximum light intensity, the rate of production of photoelectrons, $\sigma_F I$, is then of the order of 0.1 sec^{-1}. On the basis of a classical calculation by Pekar[6], which is to be discussed later in greater detail, one obtains a value of $k_v \approx 10^{-6}$ cm^3/sec and limits for the value of k_T ranging from 10^{-4} to 10^{-8} cm^3/sec. Since after the first few microseconds of bleaching n_v should be of the order of n_F one finds that the rate of capture of photoelectrons by negative-ion vacancies, $k_v n_v$ is of the order of 10^{10} sec^{-1}. From the previous experiment on the kinetics of bleaching[1] it is possible to estimate that the temperature independent part of the first stage of bleaching represents roughly 20% to 40% of the *F* centers bleached during the first stage of bleaching. It is assumed that one electron trap is filled for each *F* center bleached during the initial bleaching process. The rate of capture of photoelectrons at the electron trapping centers, $k_T n_T$, is then estimated to lie between 10^7 to 10^{10} sec^{-1}. The rate of capture of photoelectrons at negative-ion vacancies and at the traps is, therefore, much greater than the rate of production of photoelectrons at *F* centers. Consequently, the number of photoelectrons and, from Eq. (4), the rate of change of the number of photoelectrons throughout this initial bleaching process is very small.

Equations (7) and (8) can then be rewritten

$$\dot{y}=\sigma_F I(1-y)-(k_v n_{F0} y)\epsilon, \tag{9}$$

$$\dot{z}=k_T n_{F0}(1-z)\epsilon, \tag{10}$$

where $\epsilon=y-(n_{T0}/n_T)z$ is a second order term since it represents the concentration of photoelectrons. If one eliminates ϵ by taking terms up to third order into account in Eqs. (9) and (10), one arrives at an equation for y which can be solved in terms of the product It as follows:

$$\frac{(1-y)^a}{1-(n_{T0}/n_{F0})y}=\exp(bIt), \tag{11}$$

where

$$a=\frac{1-(k_T/k_v)(1-n_{T0}/n_{F0})}{n_{T0}/n_{F0}},$$

$$b=\frac{\sigma_F(k_T/k_v)(1-n_{T0}/n_{F0})}{n_{T0}/n_{F0}}.$$

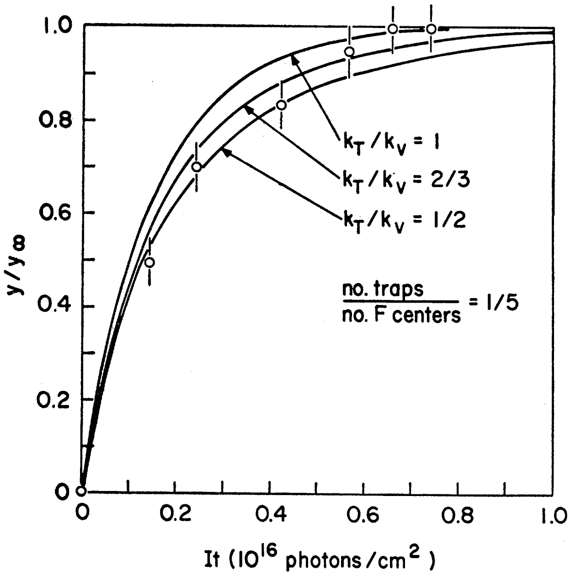

FIG. 3. Comparison of the experimental (open circles) and calculated (solid lines) variation of the number of bleached *F* centers as a function of the product of the light intensity (*I*) and the illumination time (*t*). The ratio of the number of traps to original *F* centers is assumed to be $\frac{1}{5}$.

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[5] A. Smakula, Z. Physik **59**, 603 (1930).

[6] S. I. Pekar, *Untersuchungen über die Elektronentheorie der Kristalle* (Akadamie Verlag, Berlin, 1954).

It should be observed that as the product It goes to infinity y must approach $y_\infty = n_{F0}/n_{T0}$. In Fig. 2 the experimental results are plotted together with the calculated ratio of y/y_∞ as a function of It. Figure 2 is plotted for a value of $n_{T0}/n_{F0} = \frac{1}{3}$. Figure 3 gives the results for a value of n_{T0}/n_{F0} equal to $\frac{1}{5}$. It can be seen from Figs. 2 and 3 that the general shape of the calculated curves agrees well with the experimental points, and that within the accuracy of the determination of n_{T0}/n_{F0} a good average value for k_T/k_v is about unity.

Theoretical estimates of the value of k_T/k_v are not easy to obtain, since calculations of the capture cross section of defects for mobile carriers in polar crystals are not available. Pekar[6] has given estimates based upon a classical argument. He considers the two limiting cases[7] in which the recombination rate is limited by (1) the return of the electron to the ground state of the center, and (2) the diffusive motion in the attractive field of the center.

Polar crystals are just those in which the electron mobility is low and the interaction of the mobile carriers with the lattice polarization and vibration is large. Under these circumstances, Pekar's case (2) is much more likely to correspond to conditions in KCl down to even very low temperatures. As capture coefficients Pekar gives

$$k_n(\text{neutral center}) = 1.1(4\pi\mu)(kT)^{\frac{3}{4}}(\gamma/2\epsilon^2 e^2)^{\frac{1}{4}}, \quad (12)$$

$$k_v(\text{charged center}) = (4\pi e/\epsilon)\mu, \quad (13)$$

where ϵ is the dielectric constant of the crystal, μ is the mobility of the carrier, e its charge, γ the polarizability (cm^3) of the neutral center, and k and T have their usual meaning. Using $\mu = 40$ cm^2/volt-sec,[8] $\epsilon = 5$, $\gamma \approx 5 \times 10^{-23}$ cm^3, $e = 4.8 \times 10^{-10}$ esu, and $T = 300$°K one obtains the values for k_T and k_v quoted earlier. The ratio of k_n/k_v is then about 0.05 to 0.1 at room temperature.[9] It is interesting to note that the recombination coefficient for a charged center is predicted to depend only upon its charge, and not on its detailed structure.

With this estimate of k_n/k_v and the experimentally obtained value of k_T/k_v of about unity it is possible to speculate as to the nature of the electron trapping centers responsible for the initial bleaching of F centers. The traps, like the negative-ion vacancies, may be centers of net positive charge such as M, R, and N centers minus their electrons. It is however, experimentally observed that the M, R, and N centers do not grow appreciably during the early moments of bleaching. It was observed that two small bands located at room temperature at 260 mμ and 333 mμ did disappear rapidly during the first few seconds of bleaching. Etzel[10] has tentatively assigned a band located at 254 mμ band to a transition within O$^=$ centers. It is difficult to believe, however, that O$^=$ ions should be very effective traps for electrons. It is, in fact, hard to believe that any charged centers are present in the crystal prior to bleaching, particularly since even negative-ion vacancies are unstable at room temperature.[1] Alternatively, the trapping center may be a neutral center which can trap an electron. Based on Pekar's calculations one would expect that the capture coefficient of the neutral trap would be 1 to 2 orders of magnitude smaller than that of the positively charged negative-ion vacancy. If the trapping center is a neutral trap then one is forced to the conclusion that it is located very close to the bleaching F centers. In this way the neutral trap could assume a higher than normal effective cross section. Furthermore, bleaching during the initial moments may then occur by the tunnelling of electrons from F centers to the trapping centers. For the case of tunnelling equation (11) would still apply, however, the capture coefficients would require a different interpretation.

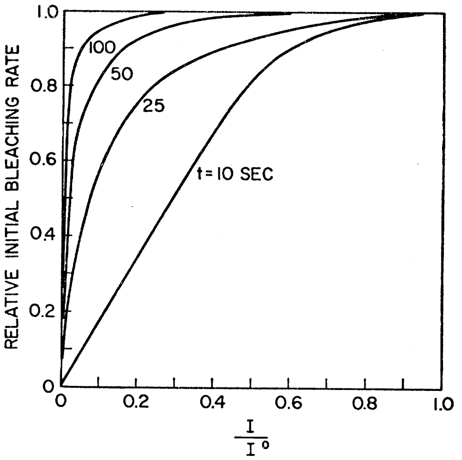

FIG. 4. The relative rate of bleaching of F centers as a function of the relative F light intensity and as a function of the illumination time (t) of bleaching.

The possibility has also been considered that the electron trap has an optical absorption at the F band, and that this absorption exists even before bleaching. For this case Eqs. (1) through (6) have to be modified to take into account two additional parameters; the number of occupied traps and the ratio of the oscillator strength of the traps to that of the F center. The solution of the equations is then qualitatively similar to that given in Eq. (11), with the addition of the two arbitrary parameters.

In theory an analysis similar to the one given above may be made for the results on the samples irradiated

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[7] These two limiting cases of recombination were first studied by Thomson and Langevin. J. J. Thomson, Phil. Mag. **47**, 337 (1921); and P. Langevin, Ann. Chem. Phys. **28**, 289, 433 (1903).

[8] A. Redfield, Phys. Rev. **91**, 244, 753 (1953).

[9] A calculation, similar to that of M. Lax (to be published), has been carried out in order to treat quantum mechanically the effect of lattice vibrations on the capture coefficient of charged electron traps (k_v). The value of k_v obtained through the quantum mechanical treatment differs from the value obtained from the classical treatment by less than one order of magnitude.

[10] H. Etzel (private communication).

into the second stage of coloration ($\alpha_{F0}=0.60$ mm^{-1}). However, a determination of the kinetics of the process which is required to determine n_{T0}/n_{F0} has not been carried out. The results of the lower curve of Fig. 1 are interpretable in terms of either a decrease in k_T/k_v or an increase in n_{T0}/n_{F0}. Since second stage coloration occurs primarily at dislocations and not near the defects created in the bulk of the crystal during the first stage of coloration,[2] it seems unlikely that k_T/k_v has been significantly altered by the second stage irradiation.

Figure 4 gives the results on the effect of light intensity on the bleaching rate on the remainder of the first stage of bleaching (10 sec$<t<$100 sec). In this figure the ratio of the rate of bleaching under a given light intensity to that under the maximum light intensity is plotted against the ratio I/I^0. The results are shown for only the first stage irradiated crystals, although a similar effect was observed in the crystals x-irradiated into the second stage of coloration. During this period of the first stage of bleaching the temperature dependent process, described in the Introduction predominates.[1] In order to treat this case Eqs. (1) through (6) would have to be modified to include the time rate of change of the accessibility of F centers and of electron trapping sites.

For bleaching times greater than 150 sec, i.e., during the second stage of bleaching,[2] the bleaching rate is already saturated at the lowest intensity used (about 1×10^{14} photons/sec cm^2). During the second stage the observed rate of bleaching of the F band is extremely small during room temperature optical bleaching, the bleaching rate in samples irradiated to $\alpha_{F0}=0.45$ mm^{-1} being about 1×10^{-3} mm^{-1}/min. If one assumes that the second stage of bleaching is not a diffusion controlled process, one may interpret the results of this stage in an analogous manner to the interpretation given to the initial moments of the first stage of bleaching. The fact that the bleaching rate during the second stage is very small and that it is essentially independent of intensity may be attributable to the possibility that the second stage centers cannot be optically ionized at room temperature. Alternatively, one may assume that the quantum efficiency for ionization of these centers does not differ greatly from that of the first stage F centers. It can then be shown when the bleaching rate saturates at intensities of less than 10^{14} photons/sec cm^2, that either the capture coefficient for the trapping center is much greater than that of the second stage centers, or that the concentration of the trapping centers is much smaller than that of the second stage center. Oberly's[11] result that the photocurrent tends toward zero during the second stage of bleaching seems to rule out the possibility that the concentration of trapping centers is very small, since in this case the mean range of electrons (Schubweg), and therefore, the photoconductivity is finite. On the other hand, an extremely small photoconductivity would result if the two centers are very close together. In this way the trapping centers would assume a very large effective capture coefficient. One is, therefore, led to conclude that the centers formed during the second stage of coloration also exist in close vicinity of each other. Results of a recent experiment by Compton and Klick[12] on the interaction of color centers during optical illumination also suggest that some color centers are closely grouped.

ACKNOWLEDGMENTS

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[11] J. J. Oberly, Phys. Rev. **84**, 1257 (1951).

[12] W. D. Compton and C. C. Klick, Phys. Rev. **112**, 1620 (1958).