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Excitonic Processes and Thermoluminescence

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Processes of defect creation by nonionizing radiation were studied by applying thermoluminescence methods. KBr crystals were irradiated at 80 K by monochromatic uv light in the region of 1800–2300 Å. Shapes of glow curves were found to differ from those obtained after x coloration. Excitation spectra of the various glow peaks as well as dose dependence of their intensities were investigated. The excitation spectrum showed maxima at the α band and on the long-wavelength tail of the fundamental absorption. Most of the glow peaks showed a linear dose dependence. The mechanism proposed by Pooley and by Hersh is extended to the case of defect creation by irradiation into a perturbed exciton state and excitation of thermoluminescence. An expression for the number of the defects created by the uv irradiation is derived as a function of the radiation dose. This expression takes into account the absorption coefficient of the crystal and, therefore, the penetration depth of the exciting monochromatic light. Experimental results were found to be in good agreement with those predicted by the model.

I. INTRODUCTION

Color-center formation in alkali halide crystals by uv radiation has been investigated by various authors.¹ Several models have been suggested to explain defect generation by ionizing and nonionizing radiation; an excitonic mechanism for the creation of F centers in alkali halides has been proposed independently by Hersh and by Pooley.² This mechanism is now extended in order to take into account creation of defects by irradiation into a perturbed exciton state, and to explain excitation of thermoluminescence (TL) by uv irradiation.

In most previous experimental investigations, crystals were irradiated with polychromatic uv light, since the low intensities of the uv light sources and the relatively low sensitivity of absorption methods did not permit the use of monochromatic uv light. The use of monochromatic light appears to be of advantage in the study of the energies connected with the creation of defects and

the processes involved.

In the present work, TL methods have been applied to study the processes of defect formation by nonionizing radiation. The relatively high sensitivity of TL compared with optical-absorption measurements enabled us to use monochromatic uv light for excitation. The excitation spectra of the main glow peaks revealed information concerning defects which were undetectable by other means under similar excitation conditions.

II. THEORETICAL MODEL

We start from the model which has been given by Pooley and by Hersh² for the creation of defects in alkali halides by irradiation into the fundamental absorption bands. We consider defect generation by uv light in the case of irradiation into the edge of the fundamental absorption as well as into the α band. We take into account the penetration depth of the exciting uv light depending on the absorption coefficient of the crystal.

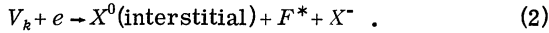
The processes occurring during irradiation may be described by the following reactions.

(a) Creation of an exciton by absorption of a photon, and its relaxation into a V_k center plus electron bounded,



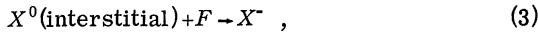
where X^- represents a halogen anion in a lattice site.

(b) Creation of a Frenkel pair by a nonradiative recombination,

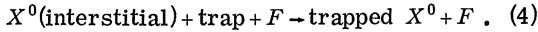


F^* is an excited state of the F center, which may decay into an F center or which may dissociate thermally. The released electron may then recombine with a hole or be trapped.

(c) The free interstitial halogen atom which is generally highly unstable at 80 K may recombine with an F center,



or be trapped, creating a stable Frenkel pair,³



It is known that at 80 K the creation of a neutral Frenkel pair ($F + X^0$) is generally predominant over creation of a charged Frenkel pair consisting of a vacancy and a negative ion.

It is suggested that upon excitation into a perturbed exciton state (α band), the crystal undergoes a similar relaxation process into the state consisting of an electron bound to a V_k center in the vicinity of a preexisting anion vacancy. These vacancies enable excitation with photons of energies lower than the energies of the fundamental absorption.

The kinetics of the processes (1)–(4) can be described by the following equations:

$$\frac{dn(V_k + e)}{dt} = \mu s - \frac{n(V_k + e)}{\tau}, \quad (5)$$

where $n(V_k + e)$ is the density of the relaxed excitons, τ is the lifetime of the relaxed exciton, s is the flux of the exciting photons per sec per unit-cross-section area, and μ is the absorption coefficient; assuming τ to be much shorter than the time of irradiation, a steady state is readily reached which results in

$$n(V_k + e) = \tau \mu s. \quad (5')$$

The changes in the densities of the F centers and the free interstitial atoms during irradiation are given by

$$\frac{dn_F}{dt} = \sigma \tau \mu s - \alpha n_F n_i, \quad (6)$$

$$\frac{dn_i}{dt} = \sigma \tau \mu s - \alpha n_F n_i - \beta m n_i, \quad (7)$$

where n_F is the density of F centers, n_i is the density of free-halogen interstitial atoms, m is the density of traps for interstitials, σ is the probability for a neutral Frenkel pair creation, α is the probability for a free interstitial to recombine with an F center, and β is the probability for trapping an interstitial.

The fact that the free X^0 interstitials are highly unstable at 80 K leads after a very short irradiation time to $dn_i/dt = 0$, and Eq. (7) becomes

$$n_i = \sigma \tau \mu s / (\alpha n_F + \beta m). \quad (7')$$

Substituting (7') in (6) gives

$$\frac{dn_F}{dt} = \frac{\sigma \tau \beta m \mu s}{\alpha n_F + \beta m}. \quad (8)$$

Farge³ has suggested that the number of traps (m) is constant and that the capture cross section of an interstitial by such traps does not vary considerably with irradiation time. In this case integration of Eq. (8) over the irradiation time (t) gives

$$\frac{1}{2} \alpha n_F^2 + \beta m n_F - \sigma \tau \beta m \mu s t = 0 \quad (9a)$$

$$\text{or} \quad n_F^2 + 2a n_F - \gamma a \mu D = 0, \quad (9b)$$

where $a = \beta m / \alpha$, $\gamma = 2\tau\sigma$, and $D = st$ is the dose of radiation.

It may be noted that Goldstein¹ had derived an equation similar to (9b), based, however, on somewhat different assumptions. He applied it to explain the experimental result that n_F was proportional to $D^{1/2}$ for large values of F -center concentration. In our case of monochromatic uv irradiation, we generally cannot assume a large F -center concentration, even for high radiation doses, since n_F depends also on the absorption coefficient and the penetration depth of the exciting light.

The general solution of (9b) is given by

$$n_F = a \left[-1 + (1 + \gamma \mu D / a)^{1/2} \right]. \quad (10)$$

At a penetration depth x , the effective dose D of the exciting light is $D = D_0 e^{-\epsilon x}$, where D_0 is the dose of the incident photons per unit-cross-section area of the crystal surface,

$$n_F = a \left[-1 + [1 + (\gamma D_0 \mu / a) e^{-\epsilon x}]^{1/2} \right]. \quad (10')$$

For a crystal of irradiated surface area A , the integration of Eq. (10') over the crystal thickness L gives the total number N_F of F centers generated by the absorbed radiation,

$$N_F = A \int_0^L n_F dx = 2aAL \frac{1}{\epsilon} \left[R - S + \ln \left(\frac{S+1}{R+1} \right) \right], \quad (11)$$

where $\epsilon = \mu L$,

$$P = \gamma D_0 / (aL) = 2\tau\sigma D_0 / (aL) ,$$

$$R = (1 + P\epsilon)^{1/2} , \quad S = (1 + P\epsilon e^{-\epsilon})^{1/2} .$$

N_F vanishes for both extreme cases

$$\lim_{\epsilon \rightarrow 0} N_F = 0 \quad (12)$$

$$\text{and } \lim_{\epsilon \rightarrow \infty} N_F = 0 , \quad (13)$$

where L is supposed to be finite and $\mu \rightarrow \infty$.

Equation (12) fits the case of wavelengths which are not absorbed by the crystal. Equation (13) fits spectral regions of extremely high absorbance and zero penetration depth. Between these extremes, N_F reaches a maximum value where $dN_F/d\epsilon = 0$. This leads to the condition

$$R + \epsilon - (1 + \epsilon)S = 2 \ln[(R + 1)/(S + 1)] . \quad (14)$$

We have solved this equation by numerical methods; P has been computed for various values of ϵ , and for various values of P , ϵ has been computed as well. It was found that no finite value of P could be obtained for $\epsilon < 2.5$ (except for the trivial case of $P=0$, which results in $N_F=0$), and that for any value of P only a value $\epsilon > 2.5$ could be found which satisfied the maximum condition (14). It might be noted that P is proportional to the dose D_0 of the exciting radiation. For our crystal of thickness $L = 2$ mm, the value of $\epsilon = 2.5$ corresponds to an absorption coefficient $\mu = 1.25 \text{ mm}^{-1}$. In such a crystal, N_F reaches a maximum for a given value of P only at an exciting wavelength where $\mu > 1.25 \text{ mm}^{-1}$. In the region of $0 < \epsilon < 2.5$, N_F increases monotonically with ϵ . Therefore, in the case of defects created by irradiation into a weak absorption band ($\epsilon < 2.5$) – like the α band in an untreated crystal – N_F varies with the wavelength in the same manner as μ . By irradiation in a spectral region of high optical density, a maximum of N_F will generally not be reached at the wavelength of the absorption peak, but will appear on the tail of the absorption band. The exact location of this excitation maximum depends, for a given crystal, on the value of P .

The expression for N_F in Eq. (11) can be expanded in powers of ϵP ;

$$N_F = \frac{1}{2} aAL(1 - e^{-\epsilon})P \left[1 - \frac{1}{8}(1 + e^{-\epsilon})\epsilon P + \dots \right] \quad (15a)$$

$$\text{or } N_F = \frac{1}{2} aAL(1 - e^{-\epsilon})P \left[1 - \delta + \dots \right] , \quad (15b)$$

where $\delta = \frac{1}{8}(1 + e^{-\epsilon})\epsilon P$.

For $\epsilon P \ll 1$, we have

$$N_F = \frac{1}{2} aAL(1 - e^{-\epsilon})P . \quad (15c)$$

The numerical computation of P from the maximum condition (14), for various values of ϵ , showed also that the increase of ϵ results in a

rapid decrease of the corresponding values of P as well as of ϵP . A few of these values of ϵ , P , ϵP , and δ are given in Table I.

By ascending on the absorption edge, ϵP easily reaches values $\epsilon P \ll 1$, and does so even for values of P somewhat greater than those given in Table I which satisfy condition (14). For example, if $\epsilon = 7$, the corresponding value is $P = 0.007552$, $\epsilon P = 0.05286$, and $\delta < 0.007$. Even if we increase P ten times the value given by the maximum condition for $\epsilon = 7$, δ remains still smaller than 0.07.

Substituting $P = 2\tau\sigma D_0 / aL$ in Eq. (15c) gives

$$N_F = A\tau\sigma(1 - e^{-\epsilon})D_0 . \quad (15d)$$

We may therefore conclude that for $\epsilon P \lesssim 0.1$, N_F is proportional to the dose of the exciting light (with an error less than 2%).

From Eq. (11), a simple expression for N_F as a function of ϵ and P can also be obtained for the case of excitation with relatively high doses. Assuming $\epsilon P \gg e^\epsilon (> 1)$, we have

$$N_F = 2aAL(1 - e^{-\epsilon/2})\epsilon^{-1/2}P^{1/2} . \quad (16)$$

This fits the previously¹ treated special case of a square-root dose dependence of N_F .

All the above expressions are developed for N_F ; however, according to the above-mentioned mechanism, it is obvious that the number of trapped interstitial atoms equals the number of F centers. In a more general case, one may take into account various F -type centers as well as various kinds of interstitial traps.

III. EXPERIMENTAL TECHNIQUES

For our experiments, KBr specimens of 9×11 -mm² cross section and about 2 mm thick were cleaved from a single Harshaw crystal. For some of the experiments, the crystals were kept in a vacuum cryostat with spectro-sil windows, and irradiated at a temperature of 80 K by monochromatic light from a 50-A Sylvania deuterium lamp, and a 0.25-m Ebert monochromator (Jarrel-Ash). The grating was blazed for 3000 Å and its linear dispersion was 33 Å/mm; the slit width was 2 mm.

TABLE I. Computed values of the parameters satisfying the maximum condition for N_F .

ϵ	P	ϵP	δ
2.6	12.64	32.87	4.414
2.8	3.222	9.022	1.196
3.0	1.604	4.812	0.6313
4.0	0.2365	0.9460	0.1204
5.0	6.554×10^{-2}	0.3277	4.124×10^{-2}
6.0	2.153×10^{-2}	0.1292	1.619×10^{-2}
7.0	7.552×10^{-3}	5.286×10^{-2}	6.614×10^{-3}
10.0	3.642×10^{-4}	3.642×10^{-3}	4.552×10^{-4}

In later experiments, the crystals were kept in a windowless cryostat attached to a 1-m normal-incident McPherson (model 225) vacuum uv monochromator. The grating was blazed for 1500 Å and its linear dispersion was 8.3 Å/mm; the slit width was 1 mm. The light source for these experiments was a 1000-W hydrogen arc lamp. The photon flux of the exciting light was monitored by a sodium-salicylate screen. The crystal was heated from 80 to about 450 K at a rate of 25 K/min.

TL was detected by an EMI 6256S photomultiplier, and recorded by an X-Y recorder with the use of a Keithley 410 micro-microammeter. The temperature was measured by a thermocouple, the emf of which was applied to the X input of the recorder.

IV. EXPERIMENTAL RESULTS

In the first series of our experiments, TL was excited in KBr crystals with polychromatic non-vacuum uv light. It was found that TL could be excited with light of wavelength shorter than 2250 Å. The shape of these glow curves differed from curves obtained from the X-irradiated crystals. Figure 1 shows, for comparison, glow curves of a KBr crystal recorded after X and after uv irradiation at 80 K. While uv excited TL has its main glow peaks at temperatures below 170 K, the main peaks after X irradiation appear at higher temperatures.

Further experiments were carried out with monochromatic uv light in the spectral region between 1800 and 2300 Å. These experiments showed that the relative intensities of the various glow peaks depended on the wavelength of the exciting light.

In Fig. 2, four glow curves for a KBr crystal excited by uv light of various wavelengths are given. These glow curves were obtained after irradiating the crystal with equal doses at 80 K.

Excitation with light in the spectral region between 1800 and 1900 Å resulted in three glow peaks at 103, 120, and 158 K (Fig. 2, curves a and b). After irradiation with lower energies, the 103 K glow peak became dominant (curves c and d). In addition to these main peaks, some weaker glow peaks appeared in the uv excited TL of KBr (at 143 and 150 K),⁴ but they were mostly covered by the stronger adjacent peaks, and their appearance depended strongly on the conditions of excitation. (For example, the 150 K could only be distinguished when excited with $\lambda > 2000$ Å and with relatively high doses.)

The excitation spectra of the main glow peaks were measured independently, with irradiation time and incident photon flux kept constant. Figure 3 shows the excitation spectra of these glow peaks. All three glow peaks had excitation maxima at 1865–1875 Å, but the 103 K glow peak had its main excitation maximum at about 2030 Å.

We have recently reported on the dose dependence of the intensities of some glow peaks in KBr. One weak glow peak (at 150 K) was found to depend quadratically on the dose of the exciting radiation when irradiated at 2030 Å.⁴ These investigations have now been extended to other glow peaks and to various exciting conditions. These glow peaks were found to depend linearly on the dose of the exciting light when the dose was changed over one to two orders of magnitude. These studies were

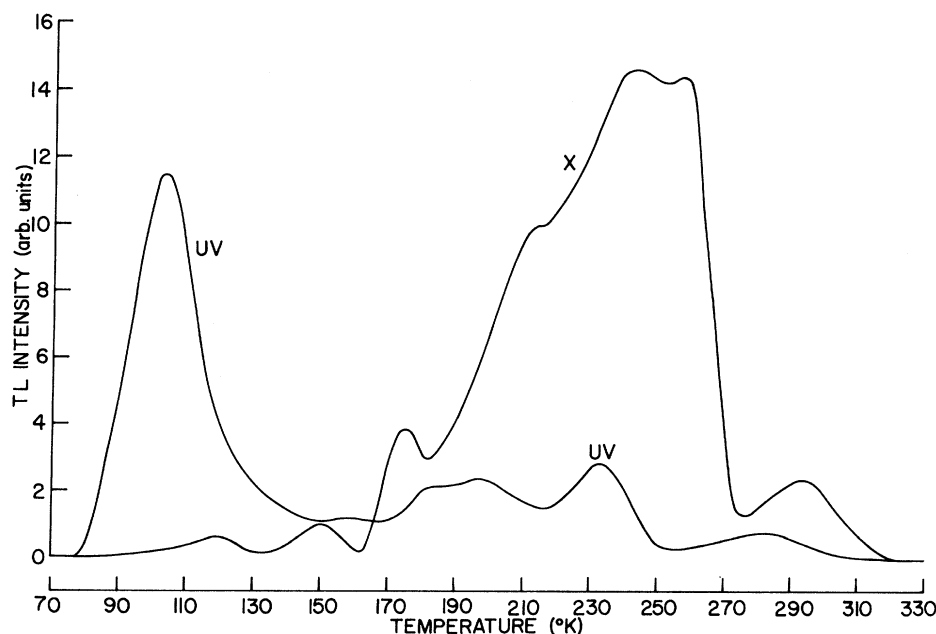


FIG. 1. Thermoluminescence of KBr. X—after x irradiation at 80 K (scale $\frac{1}{100}$). uv—after polychromatic uv irradiation at 80 K ($\lambda > 1600$ Å).

carried out separately for constant incident photon flux while varying the irradiation time, and for constant irradiation time while increasing the exciting photon flux. The measurements were taken at various exciting wavelengths.

In the course of our experiments, KBr crystals were also excited either at 300 or 240 K with uv light of various wavelengths in the region of 1900–2200 Å, and then cooled to 80 K and photostimulated into the *F* band and the main *V* bands. Figure 4 shows two glow curves of a KBr crystal excited at 240 K with light of 2030 and 1920 Å, and then photostimulated at 80 K with *F* light (6000 Å); the 120 K glow peak appeared in both cases. The 158 K glow peak became dominant after photostimulation with *F* light when excited with 1920 Å light; this peak appeared as a weak shoulder of the 150 K peak, or did not appear at all, when excited with uv light of longer wavelengths. It is worth noting that this

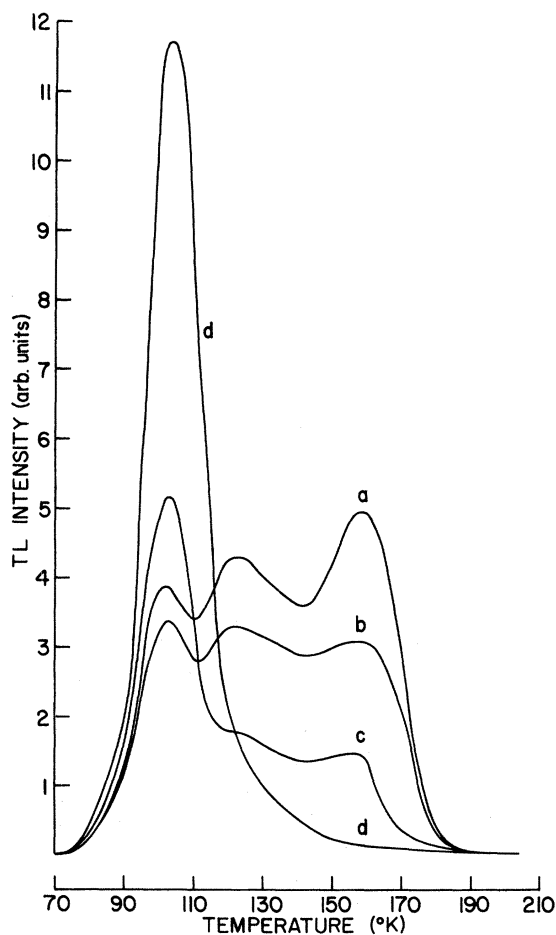


FIG. 2. Thermoluminescence of KBr after uv irradiation at 80 K with monochromatic light of (a) 1870 Å, (b) 1885 Å, (c) 1920 Å, (d) 2030 Å.

158 K peak could also be excited at 80 K with $\lambda < 1950$ Å only. Although the uv irradiation at 240 K could not directly excite a glow peak at 158 K, it seems that this peak “remembers” the wavelength of the original uv excitation even after the *F* photostimulation. The 103 K glow peak, which is the strongest after uv irradiation at 80 K, could neither be reexcited by photostimulation into the *F*- nor into any of the main known *V*-type centers. The photostimulated TL observed after excitation at 300 K showed the same low-temperature glow peaks as after excitation at 240 K, but with much weaker intensities. The TL of uv-excited crystals was observed after photostimulation even when no *F* band was detectable in the absorption spectrum.

V. DISCUSSION

A. Excitation Spectrum of TL

Thermoluminescence occurs, as known, while trapped carriers are thermally released and recombine radiatively with carriers of the opposite sign. The intensity of the glow peaks, assuming first-order kinetics, is proportional to the number of trapped carriers. Studies of the dependence of TL intensities on various parameters of the excitation conditions, such as the wavelength or the dose of irradiation, can give us relevant information about the processes involved.

The excitation spectrum of the uv-excited TL in KBr, measured in this work, was found to have maxima at about 2030 and 1870 Å. The comparison with the absorption spectrum of KBr crystals shows that the excitation maximum at 2030 Å coincides with the α band, while the second excitation peak is located on the long-wavelength tail of the first exciton band. (At 80 K, the exciton band has its peak at 1830 Å.⁵)

For a region of high absorbance, the proposed model predicts the appearance of an excitation maximum on the tail of the absorption band and not at its peak.⁶ The appearance (reported here) of a TL excitation maximum on the long-wavelength tail of the fundamental absorption fits, therefore, the prediction of the model. Figure 5 shows for comparison the measured excitation spectrum of the 158 K glow peak (curve b), and the relative values of N_F for the same spectral region, as computed from Eq. (11) (curve a). For this computation we have used the expression of the absorption coefficient

$$\mu = 2.4 \times 10^5 e^{-0.79h(\nu_{\max} - \nu) / (kT)} \text{ mm}^{-1},$$

given by Martienssen⁷ for the region near the first fundamental absorption peak in KBr, and in our case $T = 80$ K, $h\nu_{\max} = 6.77$ eV, and $L = 2$ mm. The relative values of N_F given in Fig. 5 (curve b) are

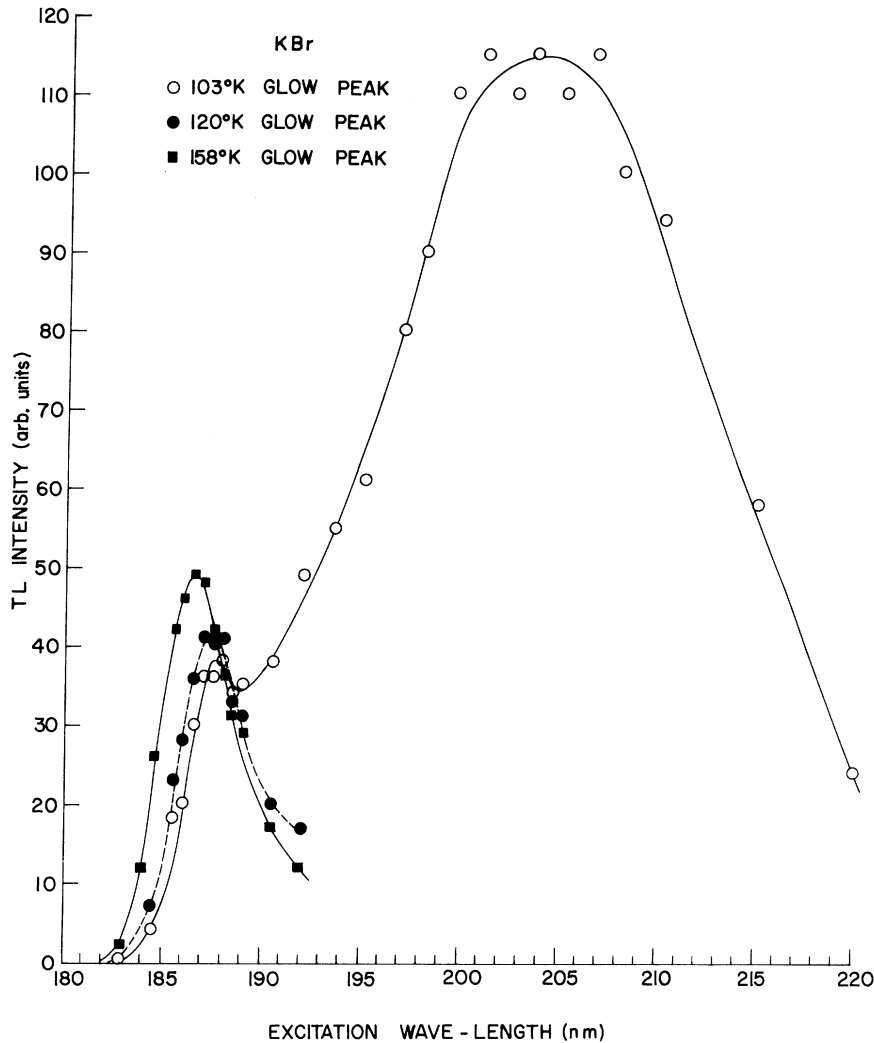


FIG. 3. Excitation spectra of various uv-excited glow peaks of KBr.

the values of $N_F/N_{F_{max}}$, where $N_{F_{max}}$ is the number of F centers for a specific P , when ϵ satisfies the maximum condition (14). The observed decrease in the excitation spectrum near the absorption peak appears to be in good agreement with the computed values in this region. The difference between these two curves at the longer wavelengths is apparently due to the fact that the computed values in this region are based on an extrapolation of Martienssen's function of μ . A comparison of these values of μ with experimental absorption curves given by Pick⁸ shows that for $\lambda \gtrsim 1860 \text{ \AA}$, Martienssen's values are significantly smaller than Pick's. In fact, approximate values of μ taken from Pick's curves give a better agreement of the computed $N_F/N_{F_{max}}$ with the excitation spectrum for $\lambda \gtrsim 1860 \text{ \AA}$. Unfortunately, the absorption curves available in the literature for this region do not reveal sufficiently exact information for a

numerical computation.

The fact that the TL has an excitation maximum at the wavelength of the α band supports the assumption that an analogous excitonic mechanism is responsible for the defect creation in the vicinity of a preexisting vacancy. The relatively small number of the preexisting vacancies appears to be sufficient for exciting TL by this process. In fact, the excitation maximum at the wavelength of the α band was found, although no α absorption band was detectable in the specimens. In our crystals, μ was less than 1 mm^{-1} at the wavelength of the α band, and therefore, ϵ was less than 2.5; this fits the case where the maximum condition (14) for N_F cannot be satisfied for any finite radiation dose. According to the proposed model, N_F and μ are, therefore, expected to vary in this region with λ in the same way, and N_F is expected to have its maximum at the wavelength of the ab-

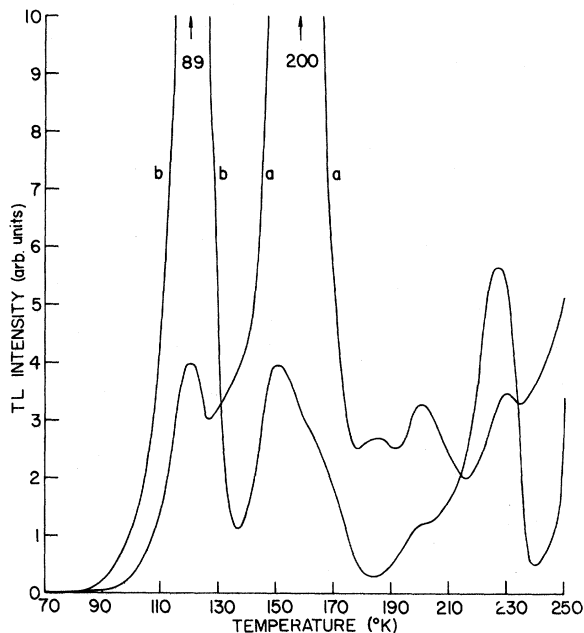


FIG. 4. Thermoluminescence of KBr excited at 240 K with uv light of (a) 1920 Å, (b) 2030 Å and then photo-stimulated at 80 K with F light (6000 Å).

sorption peak of the α band.

B. Correlation between Traps and Glow Peaks

The various glow peaks in the uv-excited TL of KBr appear to originate from different types of traps. The 150 K peak was previously⁴ found to originate from the F' center. The fact that the 120 and 158 K glow peaks appeared after photostimulation with F light at 80 K indicates that those peaks were connected with the thermal release of electrons. The experimental results showed that the 103 K glow peak did not appear after photostimulation at 80 K into the F band or into any of the known F - or V -type centers. It is, therefore, suggested that this glow peak is connected with a radiative recombination of a Frenkel pair after thermal release of the trapped interstitial. This is supported by the previously reported⁹ fact that Br interstitials in KBr crystals have an annealing stage at about 100 K.

C. Dose Dependence

The study of the dose dependence of the various glow peaks showed that the intensities of the 103-, 120- and the 158 K glow peaks depended linearly on the dose of the exciting radiation. The proposed model predicts such a linear dependence for excitation with relatively small doses, as in our case

of uv irradiation. This applies for glow peaks connected with migration of interstitials as well as for glow peaks connected with electrons released from F centers, since both types of defects are created by the same basic process.

The 103 K glow peaks showed a linear dose dependence also when excited by irradiation into the α band. From this linear dependence we conclude that no additional anion vacancies are created by this excitation process, and that the small but sufficient number of preexisting vacancies is not affected during excitation.

In order to study the difference between uv and x-ray excitations, our investigations are now being extended to higher excitation energies in the far-uv region. Preliminary experiments with $\lambda < 1700$ Å have shown that TL glow curves obtained after

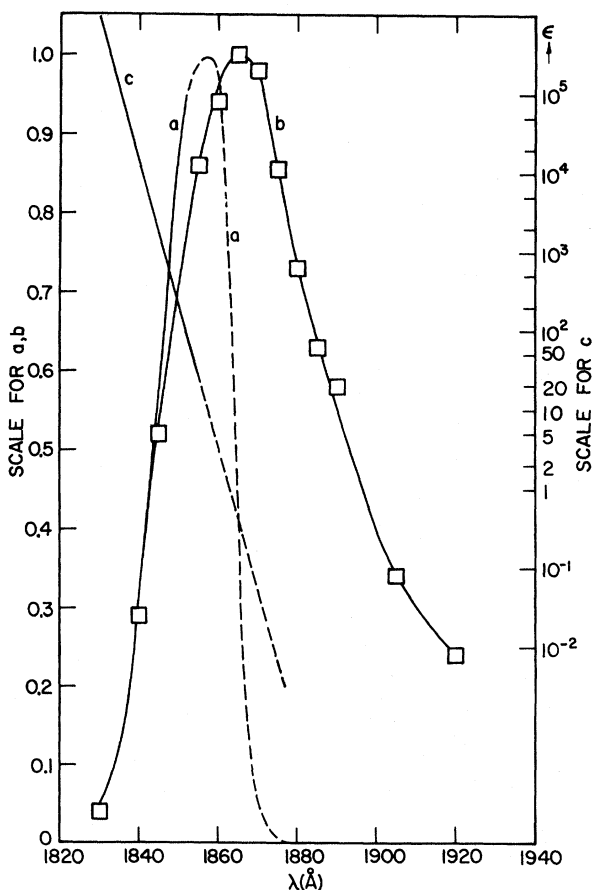


FIG. 5. (a) Excitation spectrum of the 158 K glow peak. (b) Values of $N_F/N_{F_{\max}}$ computed for $P = 7.5 \times 10^{-3}$. (c) ϵ as a function of λ as computed from Martensen's expression (Ref. 7) for $T = 80$ K, $L = 2$ mm, $h\nu_{\max} = 6.77$ eV.

excitation with photons of energies corresponding to the band-to-band transitions differ from those obtained after irradiation in the exciton bands.

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Optical Properties of NiO and CoO^{†*}

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The optical reflectance spectra of the transition-metal oxides NiO and CoO have been measured over the energy range from 1 to 26 eV. The optical constants have been derived by means of a Kramers-Krönig analysis of their reflectance spectra. Structure in reflectance is found at 4.0, 4.8, 5.9, 7.2, 8.25, 12.8, 13.6, and 17.8 eV in NiO, and at 5.5, 7.5, 12.6, and 17.5 eV in CoO. The positions of high-energy structure in their absorption coefficients is consistent with maxima in their respective optical densities of states determined from photoemission data. Two alternative interpretations are given for the structure in NiO between 4.0 and 9.0 eV. One interpretation involves oxygen *p* and nickel *d* states in localized excitations, and the other involves the nickel *d* states and the “4s” band. Distinction between models on the basis of presently available photoconductivity data is found to be questionable.

I. INTRODUCTION

The electronic structure of the low-mobility transition-metal compounds has become the subject of increased interest in recent years because of the rather diverse electrical and magnetic properties of these compounds and the recognition that they represent a considerable gap in our knowledge of the solid state.

The purpose of this work was to investigate a part of this field of study which has been the subject of considerable disagreement for some time; the electronic structure of the 3*d* transition-metal oxides. Notwithstanding the practical importance of these materials, their importance from a purely scientific view point lies in the difficulty of conceiving suitable models to explain their properties.

Studies of the optical constants in the ultraviolet and vacuum ultraviolet have proven to be a powerful method for determining details of the electronic structure of semiconductors and metals,¹⁻⁷ especially for materials for which meaningful band-structure calculations have been performed. In addition, the prior availability of the optical properties is often of considerable assistance to the theorist in making such calculations. A considerable amount of useful information can be extracted from the optical properties even though theoretical calculations are not available to assist in the interpretation. This is especially true when optical data are analyzed in conjunction with other experimental data such as photoelectron energy distributions.⁸⁻¹¹

In this paper we present the results of reflectance