Luminescence from Zero-Phonon Transitions and Oxygen in Solid Krypton*

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Luminescence from solid krypton, which has been grown from a melt, has been studied during x irradiation. Peaks near 3000 Å (4.1 eV) have been observed which are not enhanced upon selective impurity dopings, grow with x irradiation, and are only present at temperatures below 25 °K; these peaks are thought to be caused by intrinsic color centers. This luminiscence, which may be due to the excited states of the Kr_2 molecule, and the emission near 5700 Å (2.2 eV), which is attributed to an atomic oxygen impurity, can be described in terms of the theory of zero-phonon transitions which has been applied to color centers in the alkali halides.

I. INTRODUCTION

The physics of color centers in alkali halide crystals has been studied extensively for over 50 years. Since the early efforts of Pohl and his colleagues, identification of a number of color-producing centers has been made.[1] The mechanisms governing the behavior of these color centers are thought to be generally well understood. It is of interest as to whether similar centers exist for radically different materials such as rare-gas solids.[2] Solid rare gases, which are closed-shelled electronically and are bound by weak short-ranged van der Waals forces, should not contain the same type of centers as in the strongly bound, ionic alkali halide crystals. The possible exception would be the V_k molecular-type center which is formed in the alkali halides when two halogen atoms X trap a hole to form a X_2^- molecule. The analogous situation in the solid rare gases would be when two rare-gas atoms R trap a hole to form a R_2^+ molecule. This is commonly referred to as a dimer. Dimers in rare gases have been detected using mass spectroscopy,[3] vacuum-ultraviolet emission,[4,5] and recently using Raman spectra.[6] Theoretically,[7-9] it would seem possible that rare-gas dimers or V_k centers should be stable in the solid phase.

Intrinsic luminescence in crystalline krypton has been previously reported[10]; however, further investigations in this laboratory[11] have revealed that some of this luminescence may have been caused by undetected impurities in the gas samples. Careful investigation of the impurity-doped rare-gas-solid spectra[11] has identified all detectable impurities and their effect upon the luminescence. However, certain peaks in krypton, which are strongly x-ray-dose dependent, thermally quenched around 25 °K, and not enhanced with impurity dopings, appear to be intrinsic in nature. This paper reports some of the recent work on this data in the light of the V_k-type color center.

II. EXPERIMENTAL

Rare-gas crystals were grown using a technique which was perfected by the rare-gas-solids group at the University of Illinois.[12] A tube constructed from 0.005-in. Aclar[13] approximately $\frac{1}{2}$ in. long and $\frac{3}{16}$ in. in diameter was epoxied[14] between two copper blocks which could be individually controlled to within 1 °K using the appropriate on-off controllers (see Fig. 1). There was a hole in the upper copper post containing a tube which connected the Aclar growing chamber to the external gas-handling system; before a solid was grown the chamber was pumped down to 10^{-6} Torr. The solids were grown by condensing research-grade krypton[15] into a liquid and then, through the use of the temperature controllers, lowering the temperature of the lower copper post until solid filled the Aclar tube. This process, which was done at 1 atm of pressure and required nearly 1 h to complete, produced optically clear solids. The temperature was lowered to 4 °K where liquid helium was allowed to flow up and cover the sample of
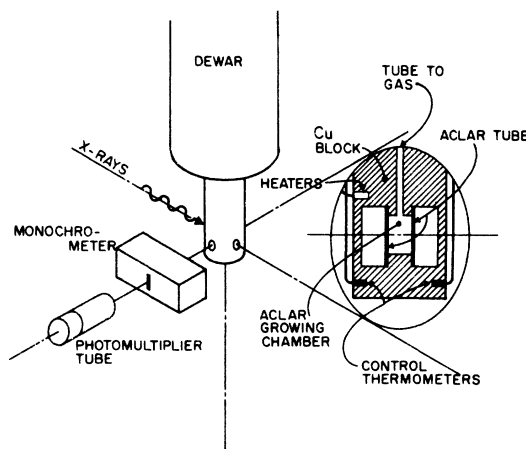

FIG. 1. Experimental apparatus for measuring luminescence from krypton solids.
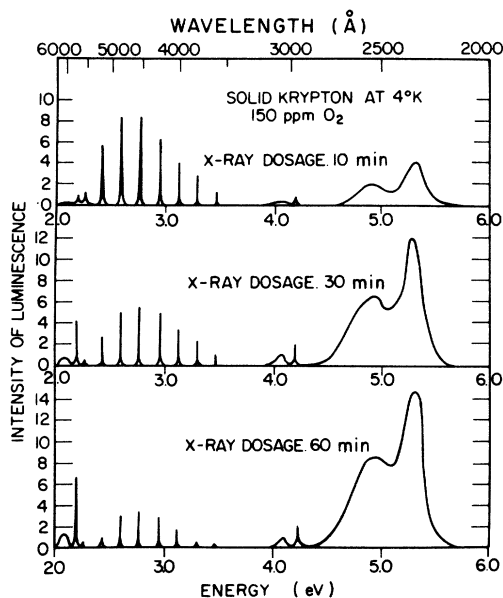
WAVELENGTH (Å)

FIG. 2. Luminescence spectra from solid krypton at 4° K containing 150 ppm of O_2 as a function of time.

krypton.[16] Temperature was measured with an (Au: 2. 1-at. % Co)-(Ag: 0. 37-at. % Au) thermocouple and a germanium cryoresistor.[17] Samples were x rayed through a beryllium window with a copper x-ray tube at 50 keV and 15 mA from approximately 2 in. Luminescence was measured as shown in Fig. 1 with the use of $\frac{1}{4}$-m monochrometer[18] and a photomultiplier tube.

III. EXPERIMENTAL RESULTS

The luminescence spectra of several krypton samples during x irradiation at 4 °K are shown as a function of time in Fig. 2. While the intensity of the luminescence of the various peaks in these spectra varies with both x-ray dosage and impurity content of the samples, the positions of these peaks remain unchanged with such variations. (Points on the spectra could be resolved within ± 10 Å.) As shown in Fig. 2, certain bands of the spectrum increase with x irradiation [peaks near 2500, 3000, and 5700 Å (5. 0, 4. 1, and 2. 2 eV)] while others tend to decrease [the sharp peaks between 3400 Å (3. 6 eV) and 5500 Å (2. 3 eV)]. All peaks which do grow, do not do so at the same rate; the complex at 3000 Å (4. 1 eV) reaches its maximum luminescence after approximately 15 min of irradiation, whereas the peaks at 2500 Å (5. 0 eV) and 5700 Å (2. 2 eV) do not appear to reach a saturation point.

As seen in the comparison of Figs. 2 and 3, there exists a direct relationship between the intensities of many of the peaks in the krypton spectrum at 4 °K and the addition of oxygen. The exception to this rule is the peak complex at 3000 Å

(4. 1 eV) which exhibits an inverse relationship between its luminescence and O_2 impurities. The position and relative spacing of the peaks between 3400 and 5500 Å (3. 6–2. 3 eV) identified them as the Herzberg bands of O_2 which are due to the forbidden $X^3\Sigma_u^+ \rightarrow A^3\Sigma_g^-$ transitions.[19]

The peaks near 2500 Å (5. 0 eV) and 5700 Å (2. 2 eV) which grow with x irradiation and are enhanced with oxygen doping appear to be due to emission from oxygen species formed from molecular oxygen upon x irradiation. By comparing with the known transitions in atomic oxygen,[20] the line at 5620 Å (2. 21 eV) appears to be due to the blue shifted $2P^4\,^1D_2 \rightarrow 2P^4\,^3P_2$ (1. 97 eV). The broadening of this peak is probably due to inhomogenous effects in the solid. The blue shifting of 0. 24 eV for the 1. 97-eV atomic-oxygen emission is in keeping with the shift of the atomic lines of krypton in the solid phase.[21] The luminescence at 2350 Å (2. 58 eV) may be due to be the blue-shifted $2P^4\,^1S_0 \rightarrow 2P^4\,^3P_0$ (4. 16-eV) transition in atomic oxygen. The shift of this transition seems too large to correctly explain this emission. Another possibility for the liminescence at 2350 Å (5. 28 eV) could be the $A^2\Pi_u \rightarrow X^2\Pi_g$ (4. 81-eV) transition in O_2^+.[19] The O_2^+ could be easily formed from O_2 upon x irradiation and the blue shift of 0. 47 eV is closer to the shifts in atomic krypton[21] than a shift attributed to atomic oxygen. The band red shifted from these peaks by a few tenths of electron volt's 5960 Å (2. 08 eV) and 2500 Å (4. 96 eV), are thought to result from electron-phonon interactions and therefore should not be observed in the gaseous data.

In addition to the oxygen doping, solids of krypton have been studied containing impurities of Xe, N_2, NO, and CO in this and other investigations.[11] With the exception of CO, which, in addition to O_2, tends to enhance the luminescence near 2500 Å (5. 0 eV), no additional impurity enhancement of the spectrum at 4 °K has been observed. As can be seen in Fig. 3, the 3000-Å (4. 1-eV) complex
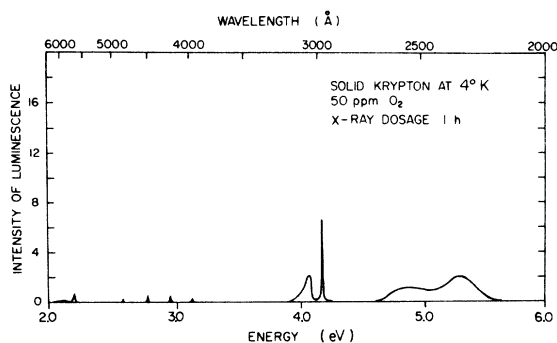

FIG. 3. Luminescence spectra from solid krypton at 4 °K containing 50 ppm of O_2 after 1 h of x irradiation.

appears to be largest in the "cleanest" of the solids. This complex has not been observed in the thin films of krypton which were prepared by depositing gas upon a cold substrate (near 20 °K) and investigated in the same manner as the bulk samples described previously. The 3000-Å (4.1-eV) complex has been only observed in samples which have been prepared from a melt of liquid krypton. It should be noted that the 5700-Å (2.2-eV) line has been observed in both thin films and bulk samples.

The growth of the peaks in the 3000-Å (4.1-eV) complex, as shown in detail in Fig. 4, has been studied with x-ray dosage; the growth of the 2950-Å (4.20-eV) line is shown in Fig. 5. The intensity of the luminescence of an individual crystal is dependent predominately upon how optically clear the solid was and what impurities were present upon growth. Excessive cracks in the solids, resulting from thermal cycling and exposure to liquid-helium temperatures for long periods of time (1 h and longer), would scatter the luminescence of the solid, therefore decreasing the amount of light which would be seen by the photomultiplier tube. To compare the growths of the luminescence of the 2950-Å (4.20-eV) peak, it was therefore necessary to normalize its luminescence in the form of

$$I(t)/I(\infty) = 1 - f(t), \qquad (1)$$

where $I(t)$ and $I(\infty)$ are the intensities of the luminescence at any time t and at $t = \infty$, respectively. $f(t)$ is the necessary function of t which will result in the correct values in Fig. 5. Trial functions for $f(t)$ were fit to the data; however, no simple form for $f(t)$ was discovered. The best candidate for the empirical fit was $e^{g(t)}$, where $g(t)$ was a polynomial containing cubic and higher terms. The growth of the 3030-Å peak was normalized in a similar fashion, and it was found to closely follow the form of the growth curve in
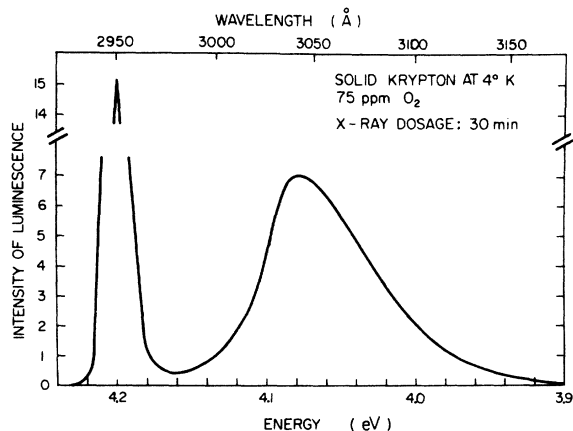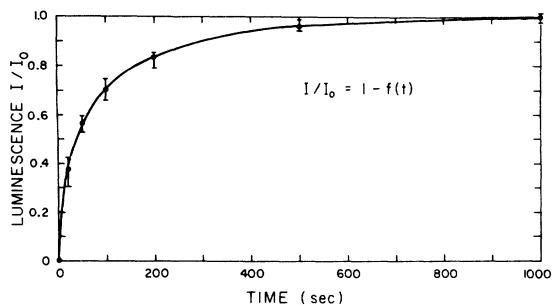

FIG. 5. Growth of the 2950-Å (4.20-eV) peak with x-ray dosage.

Fig. 5. Unfortunately, due to the large amount of uncertainty in the measurements of the 3030-Å (4.09-eV) peak, the error bars for this case were two and three times larger than those of the error bars for the 2950-Å (4.20-eV) peak in Fig. 5

At the saturation point, i.e., at times greater than 500 sec, the ratio of the 2950-Å (4.20-eV) peak to the peak at 3030 Å (4.09 eV) varied anywhere from 2–4. Although no quantitative correspondence of this ratio of the peaks was observed between any impurity present in the solid or temperature cycling, it was noted that the ratio of the 2950-Å (4.20-eV) peak to the 3030-Å peak was the largest in the "cleanest" solids.

The growth of the oxygen-enhanced peaks near 2500 Å (5.0 eV) and 5700 Å (2.2 eV) has been studied with x-ray dosage and appears in Fig. 6. As with the growth curves for the 3000-Å (4.1-eV) complex, the intensities of the luminescences are normalized for ease in analysis. The choice of normalizing the intensities at 30 min is made since a saturation intensity of the peaks (2500 and 5700 Å) is not observed in x-ray dosage of up to

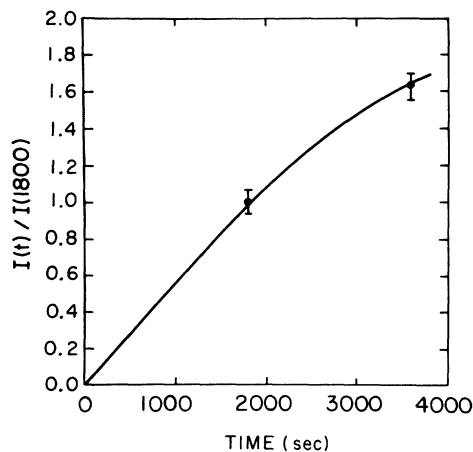FIG. 4. Luminescence complex near 3000 Å (4.1 eV).

FIG. 6. Growth of the 5700-Å (2.2-eV) and 2500-Å (5.0-eV) complexes with x-irradiation.

1 h. However, from noting the slope of the curve in Fig. 6, it is plausible that these peaks will, as with the 3000-Å (4.20-eV) complex, reach a maximum saturation intensity; this may require a few hours of x irradiation. It should be also noted that the intensity of the luminescence of the molecular-oxygen peaks (the Herzberg lines) decrease at comparable rates to the increase in luminescence of the peaks near 5700 Å (2.2 eV) and 2500 Å (5.0 eV), indicating a conversion of O_2 to O or perhaps O_2^*.

IV. DISCUSSION OF RESULTS

The peaks near 5700 Å (2.2 eV) and 3000 Å (4.1 eV) bear a strong resemblance to the luminescence from zero-phonon transitions[22] reported for certain color centers in alkali halides. A zero-phonon transition in luminescence at 0 °K consists of (i) a sharp zero-phonon peak (a transition which does not require phonons to complete) and (ii) a broad multiphonon sideband (transitions which are phonon-assisted) red shifted from the zero-phonon peak (see Figs. 4 or 7). The characteristic shape of this transition is due to the favorable position of the ground state of the excited species to the ground state of the normal molecule for this (0, 0) transition, resulting in an unusually strong zero-phonon peak. The position of the multiphonon-assisted sideband to the zero-phonon peak is determined by the electron-phonon coupling of the center. An interesting property of zero-phonon transitions is that its luminescence and absorption band may form "mirror" images about the zero-phonon peak.

Zero-phonon transitions tend to occur at temperatures much less than the Debye temperature of the host material. The predominant temperature effects of these transitions are the broadening, red shifting, and exponential decrease in intensity of the sharp zero-phonon peak with rising temperature. There may also be a growth of the phonon-assisted sideband at the expense of the zero-phonon peak and a general loss of fine structure of the entire spectra. However, since solid krypton has a relatively low Debye temperature (70 °K) and the 3000-Å (4.1-eV) complex was observed to quench at temperatures above 25 °K, the region for careful temperature study of this complex was limited as compared with previous studies.[23]

It should be noted that the observed width of the zero-phonon peak in the 3000-Å complex was determined by the bandpass of the monochromator, and it was felt that the half-width of the peak is somewhat less than the 0.03 eV that is shown in Fig. 4.

Previous authors[22] have obtained expressions governing the transition probability from the ground state of the unexcited molecule to the nth excited
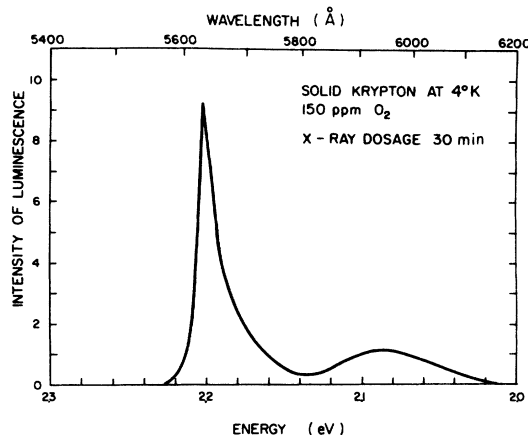

FIG. 7. Luminescence complex near 5700 Å (2.2 eV).

state of the excited molecular species at 0 °K as

$$W_{0,n} = e^{-S} S^n / n \, ! \quad , \tag{2}$$

where S is the electron-phonon coupling constant, and n is the nth excited state. The absorption spectra for this case is

$$E_n = E_0 + n \hbar \omega \quad , \tag{3}$$

where E_n is the absorption energy and E_0 is the energy of the zero-phonon line. Equation (3) describes a luminescence spectrum if the positive sign is changed to a negative sign. In both cases the peak of the phonon-assisted sideband peaks at $n \simeq S$.

S is directly related to the strength of the electron-phonon interaction which accounts for the displacement of the excited state vis-a-vis the ground state. If the electron-phonon coupling is weak (too many energy modes), S in Eq. (2) becomes the Huang-Rhys factor.

It is possible to plot the transition probability W for various S's and n's. Although this probability was calculated for absorption, the mirror-image behavior of luminescence and absorption sidebands about the zero-phonon line allow this "envelope" to also apply for luminescence. The probability calculated from Eq. (2) for a few S's are plotted in Fig. 8. It should be noticed that with the limit $S = 0$, the probability distribution W becomes a Dirac δ function at $n = 0$. As S increases, the shape of the envelope spreads out until when $S = 40$ the shape resembles a Gaussian (or Lorentzian) distribution.

It is therefore possible to fit the shape of any zero-phonon transition with the form of Eq. (2) to obtain a value for S. It should be noted that when S is very small, say less than 1, the only part of the transition that will be seen is the sharp zero-phonon peak; for higher values of S the zero-phonon peak may also be visible at $n = 0$ in Fig. 8.
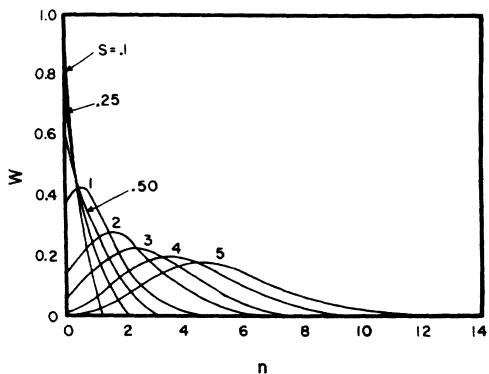
FIG. 8. Transition probabilities vs nth excited state for zero-phonon transitions.

The intensity of the luminescence of the zero-phonon peak seems to be strongly influenced by the symmetry relations governing the transitions involved and the lifetime of the individual transition.[22]

It has also been found[22] that the full width at half-maximum (FWHM) of the multiphonon sideband at 0 °K is given by

$$H(0) \simeq 2.36 S^{1/2} \hbar \omega .$$ (4)

Using this expression for the FWHM and the fact that E_n in Eq. (3) peaks about $n \simeq S$ (now called $\bar{E}$), it is possible to calculate S. The expression for S becomes

$$S = \left(\frac{E_0 - \bar{E}}{H(0)} (2.36) \right)^2 .$$ (5)

Using Eq. (5), the values for S were computed for the 3000-Å (4. 1-eV) and 5700-Å (2. 2-eV) complexes (see Table I). The values of 5.6 and 26 for the respective peaks are in keeping with the shapes of the zero-phonon transitions generated from Eq. (2). (Some of the shapes in Fig. 8 may be used for comparison with the 3000-Å and 5700-Å peaks.) The value of $S = 5.6$ for the 3000-Å (4. 1 eV) complex is close to the observed values of S for the F_3^+ (5. 3 in NaF), R_2 (3. 5 in KCl), and M'(3. 5 in LiF) bands in alkali halides.[22] The S for this complex is also close to the values for some of the rare-earth impurity centers in alkali halide crystals[24] (mostly around 4. 0). All of these transitions display weak electron-phonon coupling. The S of 26 for the 5700-Å (2. 2-eV) complex seems to indicate a stronger electron-phonon coupling than the one associated with the 3000-Å (4. 1-eV) complex. This can be compared to an S of 40 for an F center in lithium fluoride.[22]

The value of S as calculated from Eq. (5) is very sensitive to the choice of the peak and half-width positions due to the squaring operation performed on the entire expression. For example, a variation of 0. 01 eV of just one of the measurements

would result in a 10% deviation from the tabulated values of S. S, a loosely defined quantity representing the electron-phonon coupling of the excited molecule to the lattice, may not be the same locally for every point on the configuration coordinate diagram for the center. Owing to localized strains and distortions in the crystal, S may vary considerably over various points of the spectrum for the center. Many of the expressions given in this paper which use S for computation of certain properties of half-width, peak positions, etc., may require an S which differs from the average electron-phonon coupling for the center as a whole. This means that S calculated from different quantities of half-width, position of peaks, absorption intensity, etc., could vary considerably depending upon the computation made.[25] This is verified by looking at S calculated from different methods for the same center in a given alkali halide; individual S's may vary considerably from one another.[26]

From Eq. (3) it is possible to evaluate $\hbar\omega$, or vibrational spacings, for these transitions by making the substitutions of $n = S$ and $E_n = \bar{E}$ for the 3000-Å (4. 1-eV) and 5700-Å (2. 2-eV) complexes; these are given in Table I. The $\hbar\omega$ for the 3000-Å peak appears to be slightly larger (by 0. 01 eV) than the values for $\hbar\omega$ for the aggregate centers in the alkali halides given above.[22] However, these values appear to be somewhat lower than in the zero-phonon transitions of rare-earth-doped alkali halides (by a factor of $\frac{1}{2}$).

The value of vibrational spacings, $\hbar\omega$, of the centers can be computed from the average phonon energy in the solid. This average energy can be obtained from two slightly different methods. First, by using the low-temperature values for the Debye temperature in solid krypton,[27] the average phonon energy was calculated as 6 meV. In the second method, which seems to fit nicely the values for $\hbar\omega$ in the alkali halides,[23] the frequencies for the acoustic modes of the solid at the edge of the Brillouin zone are chosen for the phonon energies involved in interacting with the center. From neutron scattering measurements in krypton,[28] the phonon energies $\hbar\omega$ are between 4 and 6 meV.

TABLE I. Parameters associated with zero-phonon transitions in solid krypton (see text for explanation of symbols).

	3000-Å (4.1-eV) complex	5700-Å (2.2-eV) complex
E_0	4.20 eV	2.21 eV
$\bar{E}$	4.09 eV	2.08 eV
$H(O)$	0.11 eV	0.06 eV
S	5.6	26
$\hbar\omega$	20 meV	5 meV

Values from both of these methods seem to agree nicely with the value of $\hbar\omega$ for the 5700-Å complex. However, the value of $\hbar\omega$ for the 3000-Å complex is a factor of 4 larger than these results. The reason for this large change in the vibrational spacing is probably due to the center causing the 3000-Å (4.1-eV) luminescence. [As will be pointed out later in this paper, the luminescence at 3000 Å (4.1 eV) is thought to be from a V_k molecular-type center. For a center of this type in krypton, the vibrational spacings have been calculated and are equal to 20 meV.[9] This agrees quite nicely with the results of $\hbar\omega$ calculated from the spectra near 3000Å.]

Comparing the shape of these zero-phonon transition luminescence spectra to previously published results,[22,26] the zero-phonon peak is observed to be rather large. There are three possible reasons for this. First, as has been pointed out,[29] the oscillator strength of the zero-phonon peak at 0 °K is given by

$$f_0 = W_0(e^{-S}) , \qquad (6)$$

where W_0 is the zero-phonon transition probability and S is the electron-phonon coupling constant. If W_0 is very large, due to a large overlap of the wave functions of the ground state with those of the excited state, the zero-phonon peak would still be large. The second reason for the size of this peak is due to the half-width of the zero-phonon peak. If the peak is sufficiently narrow, its half-width would correspond to the lifetime of the state involved in the transition. From the uncertainty principle, a rather long-lifetime stable state could result in a rather sharp transition of discrete energy. The third reason is due to the sensitive behavior of the zero-phonon line in emission to the type of excitation used to produce the centers. It has been reported[30] that the width of the zero-phonon peak for color centers in the alkali halides can be varied by nearly a factor of 10 by going from x rays to α particles as the form of excitation creating the zero-phonon transition. The intensity of the 2950-Å (4.20-eV) peak could be varied with the voltage of the x-ray tube. Since the "excitation variable" is difficult to equate or correlate, the comparable size of the zero-phonon peak in luminescence does not seem to be as quantitatively understood as its counterpart in absorption.

It is also possible to fit the shape of Eq. (2) to the zero shapes of the luminescence near 3000 and 5700 Å. This results in an S and $\hbar\omega$ for these peaks as 12 and 12 meV, and 20 and 5.5 meV, respectively. The variances in S are in keeping with the different values of S calculated from methods of line position, spectrum area, etc.[26] However, since the fit of Eq. (2) to the spectrum as seen in Figs. 4 and 7 (the 3000- and 5700-Å peaks, respec-

tively) was crude, much more confidence is placed in the computation of S (and therefore $\hbar\omega$) from Eq. (5).

The 3000-Å (4.1-eV) luminescence might be due to several different things. One possibility might be some impurity which has contaminated the krypton samples. However, extensive investigation of the impurity-doped solids of krypton have been performed in this laboratory in this and other studies.[11] Krypton doped with O_2, N_2, NO, CO, and Xe has not resulted in the enhancement of the 3000-Å (4.1-eV) peak. (As mentioned previously, oxygen has been found to retard the luminescence from this complex.) It was noticed that the purest samples of krypton resulted in the largest peak complex in luminescence near 3000 Å (4.1 eV). This fact seems to suggest strongly that this complex is due to some intrinisic center in solid krypton which grows with x-ray dosage. The center which is most likely to form in the solid rare gases, as mentioned in Sec. I, is the V_k center or rare-gas dimer.

The potential curves for some excited species of rare-gas solids have been published.[31] Potential curves for excited molecules, excimers, and dimers of krypton have been calculated using similar methods as these published curves and appear in Fig. 9. One possibility for the luminescence seen at 3000 Å (4.1 eV) could be the transition from the $^2\Sigma_g^+$ excited state of the V_k center to the $^2\Sigma_u^+$ ground state. The difficulty involved in this transition is twofold; one, the energy for the $^2\Sigma_g^+ \rightarrow {}^2\Sigma_u^+$ transition is much less than the 4 eV that is required to produce the 3000-Å (4.1-eV) transition, and two, the Stokes shift, and therefore, the electron-phonon coupling constant, would be large for this transition (Fig. 9) and would not be in
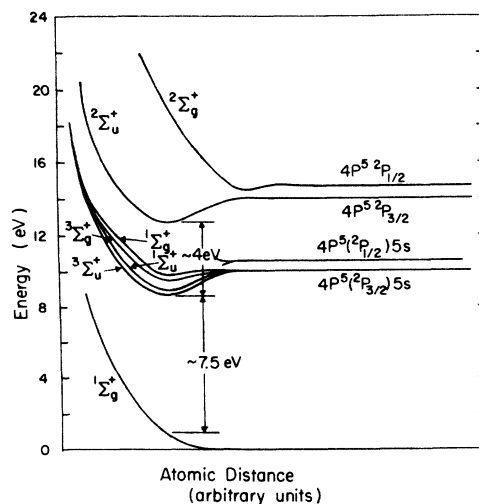

FIG. 9. Potential curves for excited krypton molecules.

keeping with the low value of S found by the prior zero-phonon anlysis.

The behavior of the complex around 3000 Å may be explained as the luminescence from the electron recombination with the V_k center. The V_k center, or a Kr_2^+ molecule, upon capturing an electron would form a highly excited form of the krypton excimer, Kr_2^*, which could then decay to the $^1\Sigma_u^+$ state of the excimer in Fig. 9 and emit a photon. The excimer could then make the transition to the ground state of the excimer—the $^1\Sigma_g^+$ state. Vacuum-ultraviolet emission from samples of krypton has been observed near 7.5 eV in this[32] and other laboratories[33] and is ascribed to the $^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ transition.

This model seems to be the best candidate for explaining the 3000-Å (4.1-eV) emission. As seen in Fig. 9, the energy of the ground state of Kr_2^+ lies about a 4 eV above the $^1\Sigma_u^+$ excited state of Kr_2^* and the shape of the curves for this transition results in a Stokes shift, and electron-phonon coupling, which is consistent with the zero-phonon analysis.

Using the nature of the V_k center in solid krypton, an explanation for the growth of its luminescence peak near 3000 Å (4.1 eV) as seen in Fig. 5 can be given. An x ray may interact with a krypton atom removing an electron and leaving an excited krypton atom, Kr^* (see Fig. 10). This, in turn, will tend to bind with a neutral krypton atom producing a stable Kr_2^+ atom. The free electron which is produced may either immediately recombine with the Kr_2^+ emitting a photon and then becoming a Kr_2^* molecule or the electron may get trapped somewhere in the solid allowing the Kr_2^+ molecule to exist and wait to recombine with another free electron. If the electron traps saturate at some rate [described by $f(t)$ as given in Eq. (1)], fewer and fewer traps would be free to trap electrons therefore allowing more electrons to recombine with the V_k centers which, in turn, emit photons. Eventually all the traps in the solids would be filled, and this would result in an equilibrium

$$T_e + Kr + Kr + h\nu \rightarrow T_e + Kr + Kr^+ + e^{-!} \begin{array}{l} \rightarrow Kr_2^+ + T_f \\ \rightarrow Kr_2^* + h\nu' \end{array}$$
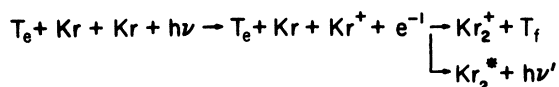
T_e = Electron Trap (Empty)
T_f = Filled Electron Trap
$h\nu$ = X-Ray
$h\nu'$ = Emitted Photon

FIG. 10. Production of Kr_2^+ from neutral Kr by x irradiation.

situation of the formation and recombination of the Kr_2^+ molecules. This would result in a constant number of V_k centers recombining with free electrons and emitting photons, hence producing the "saturated" luminescence.

To be consistent with this model the vacuum-ultraviolet luminescence from the $^1\Sigma_u^+$ state of the excimer to the $^1\Sigma_g^+$ ground state as shown in Fig. 9 should also grow with the same rate as the luminescence from the 3000-Å complex. Unfortunately this fact is not mentioned in the literature.[32,33] It has been observed by one of us (K. J. T.) that the analogous luminescence in alkali halide crystals increases with time during x irradiation. On the other hand, excitation in the exciton bands results in the same luminescence instantaneously. The luminescence of solid krypton during uv illumination has not been studied.

V. SUMMARY AND CONCLUSIONS

Luminescence at 5700 Å (2.2 eV) observed in our samples of solid krypton is due to atomic oxygen produced by dissociation of O_2. This emission shows a vibrational sideband which is due to a weak interaction of the O atom with lattice phonons. Emission near 3000 Å (4.1 eV) also has features which can be understood in terms of zero-phonon transitions. A calculation of the vibrational spacing of this emission is consistent with the vibrational spacings calculated for the Kr_2^+ molecule or V_k center.

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[1] The reader is referred to (a) F. C. Brown, *The Physics of Solids* (Benjamin, New York, 1967), Chap. 11, or (b) *Physics of Color Centers*, edited by W. B. Fowler, (Academic, New York, 1968), for excellent discussions of color centers.

[2] Solid krypton melts at approximately 115 °K as compared with KCl at 1090 °K.

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