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Luminescence induced by ion impact on alkali-halide crystals at high temperatures (−160 to 200°C)†

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A study has been made of luminescence induced by 25-keV H^+ and He^+ ion impact on pure alkali halides. The spectra generally exhibit two wide bands, the position of which depend on the type of crystal. A detailed investigation was made of the temperature and dose dependence of luminescence, and the effect of bleaching, in KCl and KBr. The peak intensity in the luminescent spectrum is independent of temperature from −160 to −70°C, rises to a maximum at about −10°C then falls monotonically for further increase in temperature. The dependence of intensity on dose is similar to published observations of V_3 center formation. The ion-induced luminescence is not influenced by irradiating the crystal with light in the F band or by irradiating with white light. We propose that the ion-induced luminescence is due to the recombination of electrons from the conduction band with V_3 and V_4 hole centers. This proposed model is consistent with the known energies of V_3 and V_4 centers. After the surface was deliberately exposed to O_2 we also observe an additional band characteristic of O_2^-.

I. INTRODUCTION

The interaction of ionizing radiation with the solid state causes electron excitations in the form of electron-hole pairs or excitons; these subsequently decay either by a nonradiative transition with the formation of phonons and lattice defects, or by radiative transitions leading to luminescence. Intrinsic luminescence of alkali halides has been extensive investigated (see, for example, the pioneering work in Refs. 1–4); this is a fundamental luminescence associated with recombination of excited electrons with self-trapped holes (V_k centers). Intrinsic luminescence is observed for temperatures where the V_k center is stable, and for most alkali halides the radiative efficiencies and lifetimes of V_k centers begin to fall off strongly at temperatures above 100 °K due to nonradiative recombination.[4] Although efficiency of intrinsic luminescence is relatively low at temperatures of 150 °K and above, Ikeya and Crawford[5] observed a new band of luminescence in NaCl at 310 nm, which is not quenched at temperatures of 150 °K and above. They suggest that this band is associated with electron recombinations with the V_k center at some unknown impurity or by electron recombination at some type of V center formed by irradiation at room temperature. Luminescence induced by electron impact on alkali halides at 90–300 °K temperatures was extensively studied by Pinard and co-workers.[6,7] They proposed a mechanism where F centers are responsible for luminescence and quenching is related to V_3 and V_4 centers. In a study of x-ray induced luminescence at high temperatures in NaCl, Spicer[8] suggests that the luminescence centers are of the V_2- and V_4-type and emission occurs as electrons fall into these centers. Other published studies of luminescence in alkali halides at high temperatures include work on thermoluminescence,[9-11] aquoluminescence,[12,13] neutron-induced luminescence,[14] and x-ray induced luminescence in string crystals.[15,16] Previous work on luminescence induced by energetic ion impact on high-temperature crystals is restricted to the work of Alekseev *et al.*[17] concerning bombardment of KCl and NaCl by H^+; here the emission was associated with water molecules in the excited triplet state, present in the crystals as uncontrolled impurities.

In the present paper we investigate luminescence of certain alkali halides induced by the impact of H^+ and He^+ ions with energies of 5–25 keV. Targets of principal interest in this work were NaCl, NaF, KCl, and KBr; various target temperatures in the range − 160 to 200 °C were employed. The high density of electron excitation close to the target surface causes a high efficiency for defect generation in the cation sublattice and the formation of hole centers that are stable at room temperature.

II. EXPERIMENTAL PROCEDURE

The apparatus used for this work is essentially the same as that previously described for studies of light emission when ions strike metal surfaces[18]; we shall therefore give only a very brief description here. The ions are formed in an rf discharge source, accelerated and mass analyzed before being collimated and directed onto the target. Light emission from the point of beam impact on the target was viewed by a conventional scanning monochromator observing through a sapphire window. The monochromator axis was perpendicular to the direction of the incident beam; the angle between the beam and the target surface normal could be varied but was kept at 45° for the experiments described here. The detection sensitivity of the optical system had been previously calibrated utilizing a standard tungsten filament lamp of known emissive power. The target samples were single crystals of alkali halides supplied by the Naval Research Laboratory (Washington, D. C.); they had been zone refined and had a nominal total impurity level of a few ppm or less. The samples were cleaved to a size of approximately $10 \times 6 \times 1$ mm immediately before introduction into the vacuum system. The target was mounted on a standard manipulator by Varian, providing three axes of translational motion and one axis of rotation. A specially designed target holder was employed that had a filament for heating the target region and tubes to conduct liquid nitrogen and thereby provide cooling. A number of thermocouples were provided to measure the temperature on the bombarded face of the crystal. The target chamber provided a vacuum environment with a base pressure of around 10^{-9} Torr for the work described here. After introduction into the vacuum system the targets were annealed at a temperature of 400 °C for at least 1 h in an attempt to remove surface contamination and to anneal defects in the crystal. The area of the target irradiated by the ion beam was approximately 5 mm^2 and the beam current density was generally about 10 $\mu\mathrm{A/cm}^2$; at these current densities there was no evidence of target surface charging or electrical breakdown on the surface. Tests showed that reducing the ion beam current density by two orders of magnitude did not change the shape of the observed spectra; moreover the intensity of the spectrum was linearly proportional to beam current throughout this range. We would note that the average depth of penetration of a 25-keV H^+ ion in KCl is about 400 nm; for a 25-keV He^+ ion the depth is about 150 nm.[19] Thus, the region of excitation is very close to the surface, in contrast to studies of luminescence under x-ray and uv photon excitation where much greater penetration depths are involved.

This work was primarily concerned with the impact of H^+ and He^+ ions on alkali halides; the observed spectra were the broad bands of luminescence that we shall discuss shortly, with some line emission in the sodium-*D* when crystals containing Na were employed; this sodium emission is from sputtered atoms in excited states. Some preliminary experiments were performed with neutral hydrogen beams which gave precisely the same spectra as for H^+ and He^+ impact. We also used Ar^+ beams and observed again the same basic luminescence spectrum but with strongly enhanced emissions from sputtered alkali atoms. Spectra induced by H^+ and He^+ impact were essentially the same for new crystals and for crystals that had suffered a preliminary bombardment with Ar^+; since the argon beam will readily sputter the surface this observation suggests that surface contamination did not strongly contribute to the observed emission spectra. Some preliminary experiments were also performed using crystals supplied by the Harshaw Chemical Co. and stated to be of optical purity; the observed spectra were not significantly different from those observed with the higher-purity crystals supplied by the Naval Research Laboratory. Crystals from the latter source were employed for all the detailed measurements presented here.

Various types of data are presented here. We have recordings of the ion-induced luminescence spectra to display the relevant spectral features. We show how certain of the features vary with the temperature of the target and with the dose to which the target has been subjected. In studies of the dose dependence we measure the intensity as a function of time under continuous bombardment by a beam of constant current density. We have no knowledge of the particle density distribution in the ion beam; if inhomogeneities were present then the local dose rate might differ significantly from the dose rate integrated over the ion beam's cross sectional area. Consequently, we consider it more accurate to present data as a function of the measured parameter, time, rather than the derived parameter of dose.

III. RESULTS AND DISCUSSION

In Figs. 1 and 2 are shown spectra induced by ion beam impact on targets of KCl, KBr, NaCl, and NaF; the reader is referred to the captions for the precise conditions of bombardment in each case. The spectra are corrected for the variation of relative sensitivity with wavelength but have not been placed on an absolute scale. The spectra are typical for these samples and remain essentially unchanged in basic shape if one alters beam energy or interchanges protons and He^+ ions; such changes, however, do alter the intensity of the emission. The spectra are wide luminescent bands varying in shape between the various crystals; in addition for the NaCl crystal we observe a narrow emission line at the NaD wavelength corresponding to atomic line emission from sputtered sodium atoms. In our following discussions we shall concentrate principally on the KCl and KBr spectra and con-

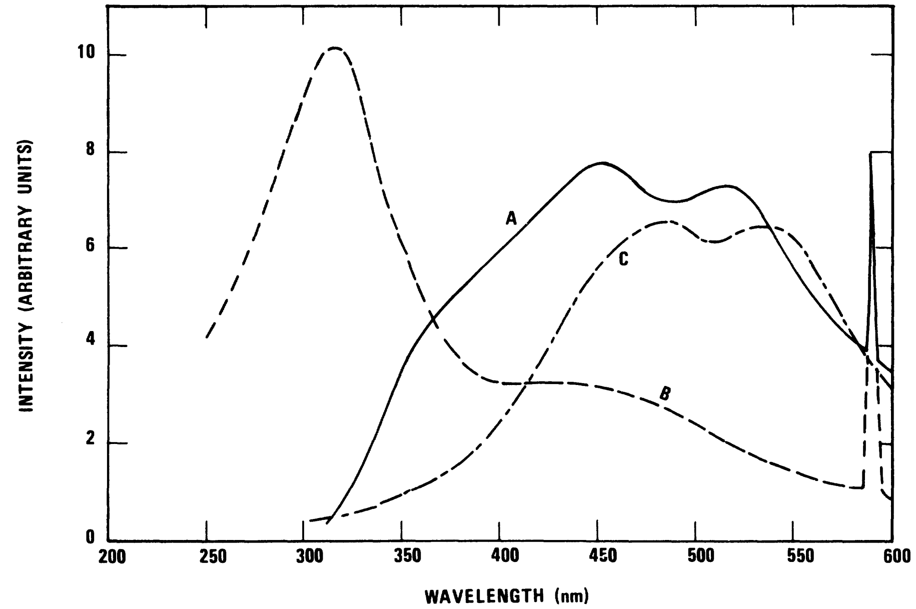

FIG. 1. Luminescence spectra of certain alkali halides at room temperature under bombardment by 25-keV projectiles. A, NaCl bombarded by a 10-μA/cm^2 H$^+$ beam at a temperature of 20 °C; B, NaF bombardment by a 6-μA/cm^2 He$^+$ beam at a temperature of 22 °C; C, KBr bombarded at a 10-μA/cm^2 H$^+$ beam at a temperature of 22 °C.

sider in detail the effects of annealing, temperature variation, and dose.

An initial test was made to determine whether any of the band spectrum was linked to impurities. We recorded the ion-induced luminescence spectrum from KCl and KBr crystals both in their freshly cleaved state before annealing and also after annealing for 5 h at 450 °C in the 10^{-9}-Torr vacuum environment. We found that annealing caused a substantial reduction of intensity at wavelengths around 530 nm, suggesting a band at this point associated with impurities. To confirm this we exposed annealed samples to nitrogen and oxygen gas for 5 min or more at a pressure of 10^{-6} Torr. Nitrogen caused no change to the spectrum but oxygen caused a rise of intensity at 530 nm by a factor of 3 and restored the spectrum to the form observed before annealing. Figure 3 shows a spectrum of KBr after oxygen absorption which should be compared with the typical spectrum of an annealed sample shown as Fig. 1(C). The annealed sample shows a small residual peak at 530

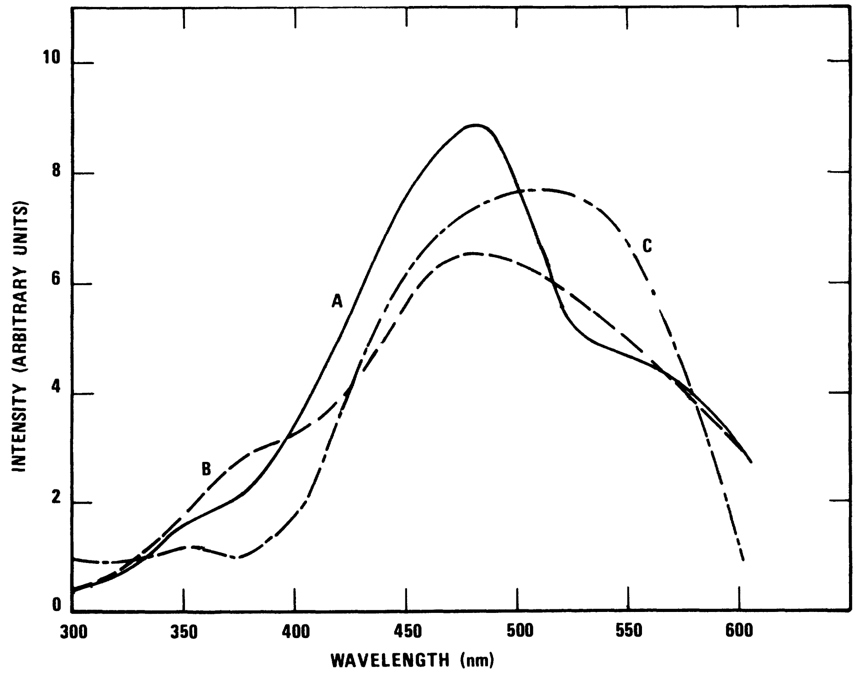

FIG. 2. Luminescence spectra of KCl and KBr at low temperature under bombardment by a 10-μA/cm^2 beam of 25-keV H$^+$ ions. A, KCl at −29 °C; B, KCl at −50 °C; C, KBr at −150 °C.

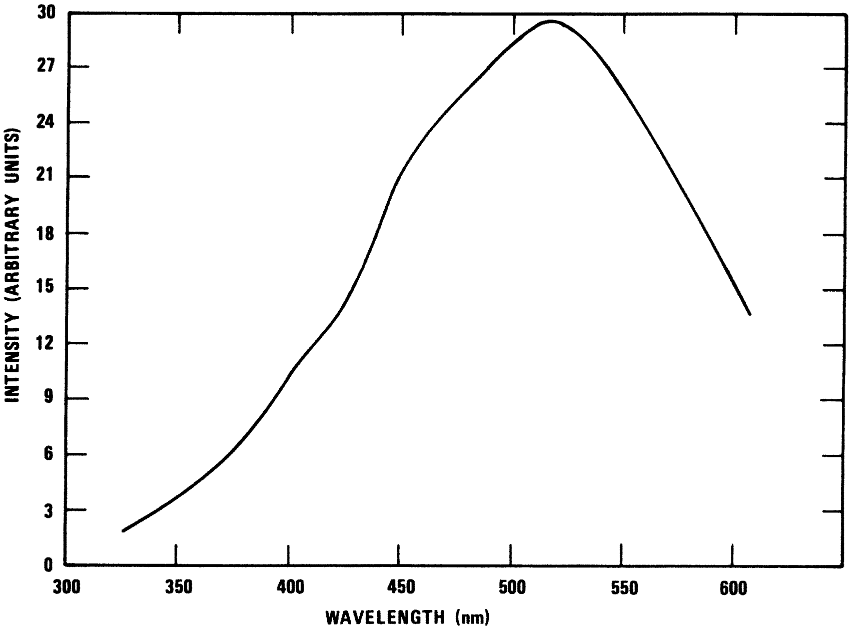

FIG. 3. Luminescence spectrum of KBr after absorption of O_2 at 10^{-6} Torr; projectile beam is 25-keV He^+ at a current density of 6 $\mu A/cm^2$ and target temperature is 29 °C.

nm but the sample with oxygen exposure is dominated by the 530-nm peak which covers and obscures the peak at 480 nm. Similar results are found with KCl and NaCl samples. We believe that the 530-nm band is due to oxygen impurities on the surface. Rolfe *et al.*[20] have studied the fluorescence of NaCl, KCl, and KBr doped with O_2^- and find a band which peaks at 530 to 550 nm, depending on the crystal; we do not, however, observe the vibrational structure seen when O_2^- is a substitutional impurity.[20] In the work that follows all crystals were first annealed to a temperature of 400 °C for 1 h or more to reduce or remove the influence of the oxygen contamination.

The most significant features of the room-temperature spectra of KCl and KBr are peaks at 480 and 500 nm, respectively; we shall later show that these are due to recombination of electrons from the conduction band with V_3 centers. At low temperatures (Fig. 2) we also observe for these same targets a weak peak at lower wavelengths, 370 nm for KCl and 350 nm for KBr; we shall later show that these peaks are due to recombination of conduction band electrons with V_4 centers. The low-wavelength peaks are strongly overlapped by the more-intense high-wavelength peak and show up on the spectra as only weak shoulders; they are, however quite reproducible.

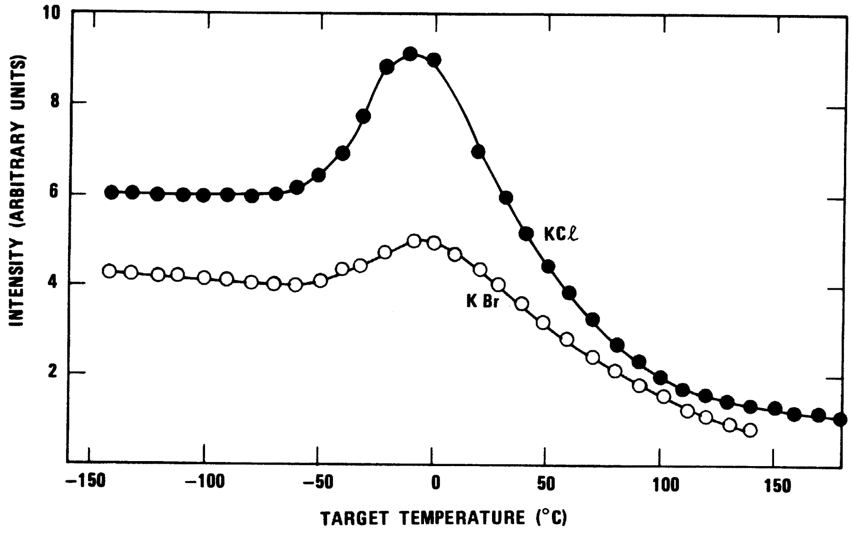

FIG. 4. Dependence of the luminescence intensity on target temperature. Targets are KCl and KBr; bombarding beam is 25-keV H^+ at a density of 10 $\mu A/cm^2$. Intensity is measured at the wavelength of maximum intensity which for KCl is 480 nm and for KBr is 500 nm.

In Fig. 4 we show measurements of luminescent intensity as a function of temperature for KCl and KBr crystals. The intensity is measured at 480 nm for KCl and 500 nm for KBr with a spectral resolution of 4.8 nm; these wavelengths correspond to the peaks of intensity in these spectra. It was found that the ion beam impacting on a crystal at low temperatures could cause a significant temperature rise. Consequently, the ion beam was pulsed on for only 2 sec at each temperature in order that temperature rise should be kept less than 1 °C. Figure 4 shows that luminescent intensity is constant as temperature rises from – 150 to about – 50 °C then rises to a weak maximum at about – 10 °C and decreases for further increase in temperature. Provided the crystal had been properly annealed before commencing the measurement we found no difference between data taken as temperature increased and data taken with decreasing temperatures.

If the luminescence centers are lattice defects arising during ion bombardment, then a study of intensity as a function of dose should represent the formation of the relevant radiation defects. To study such behavior an annealed crystal was bombarded continuously for a period of 10–20 min using a H^+ beam of 10-μA/cm^2 flux density. A continuous record of intensity as a function of time, and therefore dose, was performed. Figures 5 and 6 show the results for KBr and KCl crystals at room temperature and at a lower temperature. Low-temperature behavior (Fig. 5) shows three distinct regions. First a rapid decrease of intensity over a period of 1 min; secondly a rising intensity extending over a bombardment time of 3–8 min, depending on the sample; finally the third region is a very slow decline of intensity which appears to continue indefinitely. By contrast the room-temperature behavior (Fig. 6) is an initial rapid rise, followed by a rapid fall and finally at bombardment time of 8 min or more a slow decline that continues indefinitely.

In the studies of dose dependence (Figs. 5 and 6) there are regions where intensity increases as a function of dose; these suggest that the centers responsible for luminescence are created by ion bombardment. However, the intensity of luminescence is not zero at the commencement of bombardment so that some luminescent centers are already present in the unbombarded crystal despite the preliminary annealing procedure. The fact that intensity is a function of temperature shows that the formation, and the stability, of the defects responsible for luminescence is temperature dependent. It is known that during irradiation of KBr and KCl at temperatures close to room temperature one forms[21] stable electron centers of the F and F_2 (M) types and also hole defects of the V_3 type (this center being designated V_x by Lushchik *et al.*[16]). In order to try to separate the roles of these different centers we performed some simple light bleaching experiments. First the crystals were bombarded with H^+ ions for a time of 10 min or more so that the luminescence intensity corresponded to a point on Fig. 6 in the final section of the dose dependence where intensity decreases slowly as dose is increased. Then, with the ion beam removed, the crystal was exposed to light in the F-band absorption region provided by a tungsten filament lamp and suitable ab-

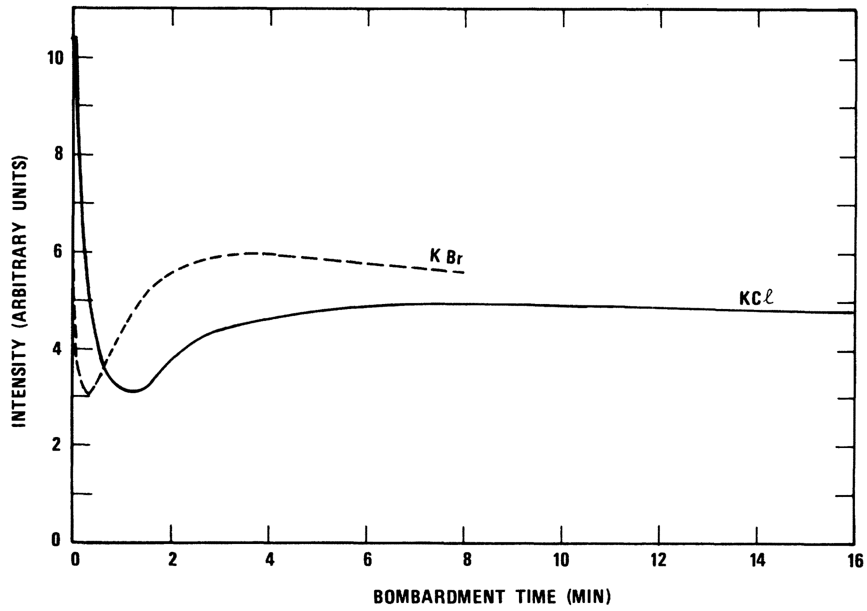

FIG. 5. Dependence of luminescence intensity on dose for targets at low temperature. Targets are KCl at – 135 °C and KBr at – 150 °C; bombarding beam is 25-keV H^+ at a density of 10 μA/cm^2. Intensity is measured at the wavelength of maximum intensity which for KCl is 480 nm and for KBr is 500 nm.

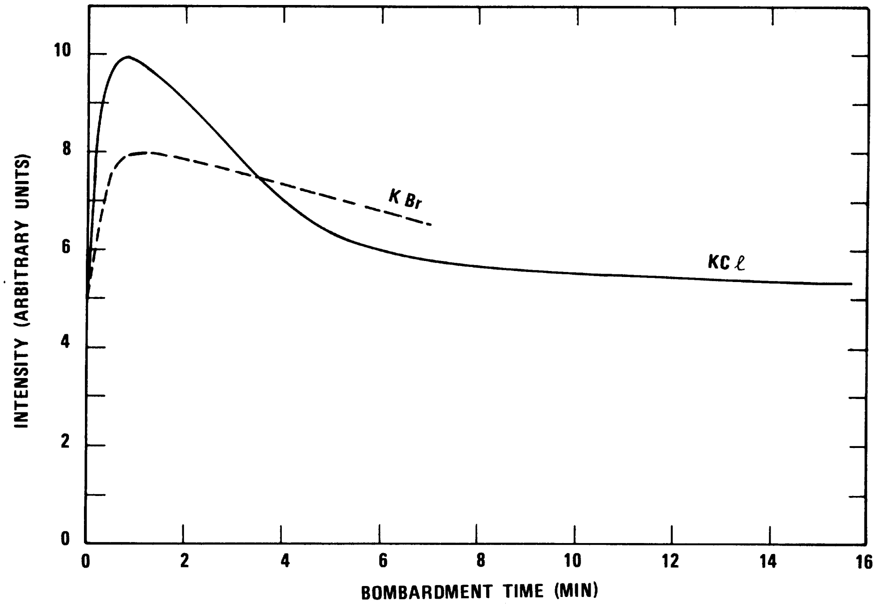

FIG. 6. Dependence of luminescence intensity on dose for targets at room temperature (22 °C). Targets are KCl and KBr; bombarding beam is 25-keV H^+ at a density of 10 $\mu A/cm^2$. Intensity is measured at the wavelength of maximum intensity which for KCl is 480 nm and for KBr is 500 nm.

sorption filters; we used 560 nm for KCl and 620 nm for KBr with a bandwidth of 140 nm in both cases. The bleaching was terminated after 30 min and ion bombardment recommenced. The intensity of the ion-induced luminescence was unchanged by the attempt of F-center bleaching. We also exposed the crystal to unfiltered white light which should bleach more complicated electron centers; again no effect was observed. Thus no effect of bleaching was found and we conclude that the centers of luminescence can be V_3 centers which are known[21] not to be bleached by white light.

We propose that the V_3 center is responsible for the principal luminescent intensity at 480 nm in KCl [Figs. 1(C) and 2(C)] and 500 nm in KBr [Figs. 2(A) and 2(B)]; it is known[21,22] that the V_3 center is stable up to 200 °C. At low temperatures we also observe a small peak at 370 nm in KCl and 350 nm in KBr [see Figs. 2(B) and 2(C)]; we propose that the V_4 center is responsible for this feature. The low-wavelength peak does not appear to be connected with impurities and as temperature is raised the feature is no longer apparent. It is known[23] that at temperatures below $-30\,°C$ the V_4 center occurs in addition to the V_3 center. However, at all temperatures considered here the luminescence we identify as due to V_3 centers, predominates. In Fig. 7 are shown the structures postulated for the V_3 and V_4 centers.[16,22] The X_3^- molecule occupies a divacancy to form a V_4 centers, and the X_3^- molecule occupies one cation and two anion vacancies to form the V_3 center. If, as we suggest, the V_3 and V_4 centers are responsible for these emission bands then the sum of energy of emitted photon and the energy of V_3- and V_4-center photon absorption, should equal the band-to-band energy. In Fig. 7 we show an energy level scheme appropriate to KCl with the suggested radiative recombination transition. In Table I we list the band-gap energies for KCl, KBr, and NaCl with the energy of photon emission which we identify as due to recombination of electrons with the V_3 and V_4 centers; also listed are the photon energies of maximum absorption ascribed by others[26,28] as due to the V_3 and V_4 centers. In KCl the band gap is quoted[24] as 8.5 eV and the energies for photoabsorption by V_3 and V_4 centers are 5.85 and 5.16 eV, respectively[26,28]; thus the predicted energies of photon emission in recombination of

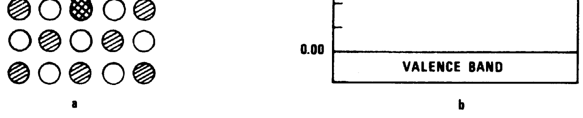

FIG. 7. Diagram of the structure ascribed to V_3 and V_4 centers with an energy level diagram for KCl showing the position of the energy levels associated with such centers.

TABLE I. Known band-gap energies and known photon energies for absorption maxima in the V_3 and V_4 bands presented with the photon energies (and wavelengths) of the peak intensity observed in the present luminescence studies. Band I is the high-wavelength band we ascribe to the V_3 center and band II is the low-wavelength band we ascribe to the V_4 center.

Sample	Energy gap (eV)	Absorption-band maxima (eV) V_3	Absorption-band maxima (eV) V_4	Observed luminescent band maxima Band I Energy (eV)	Band I Wavelength (nm)	Band II Energy (eV)	Band II Wavelength (nm)
NaCl	8.6[a]	5.9[b]	5.56[c]	2.76	450	3.31	375
KBr	7.8[a]	5.35[c]	4.5[d]	2.48	500	3.54	350
KCl	8.5[a]	5.85[c]	5.16[e]	2.58	480	3.35	370

[a] Reference 24.
[b] Reference 25.
[c] Reference 26.
[d] Reference 27.
[e] Reference 28.

electrons with V_3 and V_4 centers are 2.65 and 3.34 eV, respectively. Hence we expect emission at 468 nm for the V_3 center and 371 nm for the V_4 center; quite close to our observed peaks at 480 and 370 nm. This reinforces our conclusion that the observed luminescence is due predominantly to recombination of electrons with V_3 centers and that at low temperatures there is an additional small feature caused by recombination of electrons with V_4 centers.

It is difficult to make precise statements about the width of our observed luminescence bands since there is considerable overlap between the prominent V_3 band, the weak V_4 band and residual effects of the O_2^- impurity band. However, a rough estimate of the V_3 bandwidth at half-maximum for KCl [Fig. 2(A)] is 1.1 eV; this is consistent with the width of the V_3 absorption band which is about 1.2 eV in the measurements of Seretlo.[21]

With the identification of the emission as being due to electron recombination with V_3 and V_4 centers we should now be in a position to understand the dependence of intensity on temperature and irradiation dose. The intensity of the ion-induced luminescence will undoubtedly depend on the rate of electron excitation to the conduction band and on nonradiative decays of such electrons; also intensity will depend on the density of relevant recombination centers through their rates of creation and rates of annealing. Thus the relationship of luminescent intensity to dose and temperature is more complex than the relationship of directly measured V_3- and V_4-center density to these same experimental parameters. It would be presumptuous, and possibly misleading, to attempt a modeling of the phenomenon based only on the measured parameter of intensity; supporting information on the directly measured defect-center concentrations would be necessary in order to develop a reliable quantitative understanding. Nevertheless a general qualitative explanation may be achieved by studying the close correlations between the present work and previously published direct measurement of F-, V_3-, and V_4-center densities induced by x-ray, electron, and ion irradiation. We should note that V_3- and V_4-type centers are complementary to the F center and should therefore exhibit the same rate of formation with dose. The ion fluxes used in these studies (10 $\mu A/cm^2$) represent a rather high dose rate compared with previous studies of defect-center concentration induced by x-ray irradiation. In the work of Alekseev[17] on bombardment of NaCl by 30-keV H^+ it was found that the F-center concentration saturated at 5.35×10^{18} cm^{-3}. By comparison the studies of F-center formation under x-ray irradiation by Seretlo[21] involved a maximum F-center density of 1.5×10^{17} cm^{-3} in the irradiated sample; most irradiations were smaller.

Hughes and Pooley[29] have studied F center growth in KCl under bombardment by protons of 100-keV energy and above at high doses. F-center concentration increases to a saturation and then decreases with further increase of dose. This behavior is explained in terms of a spontaneous recombination (athermal annealing) of interstitials and vacancies. Two competing mechanisms are involved.[29] In the first, one argues that an interstitial (or vacancy) formed within some critical distance of a vacancy (or interstitial) will recombine so that no new defect center is produced. The second mechanism is a "back reaction" where F centers diffuse and either recombine with interstitials they encounter or else form F center aggregates. These mechanisms together can predict a rise in F center (and hence V_3 and V_4 center) concentration, followed by saturation, and a subsequent decrease. We observe such behavior for luminescence in room-temperature irradiation (Fig. 6) and for most of the low-temperature irradiation (Fig. 5); thus emission intensity mirrors the expected behavior of V_3- and V_4-center density. We note that Hughes and Pooley[29] find F-center concentration to saturate at a dose of about 10^{19} ions/m^2 for 100-keV impact at room temperature. In comparison, our data for 25-keV H^+ impact show saturation at a dose of about 4×10^{19} ions/m^2 at room temperature and 2×10^{20} ions/m^2 at -150 °C; thus our doses for saturation of luminescence are quite comparable with the previously observed[29] dose for saturation of F-center concentration. We can provide no explanation of the low-dose behavior in Fig. 5 where an initial rapid decrease of intensity is observed. However we note that similar behavior is seen in cathodoluminescence studies by Nouailhat *et al.*,[7] and in conductivity studies of string crystals by Melik-Gaikazyan *et al.*[15] This behavior has been ascribed[15] to the destruction of preirradiation defects.

Neglecting the effects of nonradiative electron transitions, the luminescence intensity as a function of temperature (Fig. 4) should mirror the V_3-center concentration. Seretlo[21] has studied thermal annealing of V_3 centers that were created by x-ray irradiation. For the highest irradiation densities utilized, Seretlo observes the V_3-center concentration to decrease generally monotonically with temperature above 30 °C, with the exception of a small unexplained peak at 70 °C. Our data on luminescence intensity of the V_3 band as a function of temperature above 0 °C show essentially the same behavior, apart from the unexplained peak. At temperatures below -20 °C our intensity in the V_3 band decreases and becomes constant. In this temperature region we observe increasing prominence of the low-wavelength emission band ascribed to recombination on V_4 centers; the V_4 center is, of course, an alternative final state for displaced atoms. We conjecture that the sum of V_3- and V_4-center concentrations may remain relatively constant at low temperatures but that the V_4 centers assume greater importance than at room temperatures and the V_3-center luminescence therefore decreases.

IV. CONCLUSION

The luminescence induced by impact of 25-keV H^+ and He^+ ions on KCl and KBr consists of an intense broad band peaking at around 500 nm. We identify this band as due to electron recombination with V_3 centers. At low temperatures there is a second weak feature around 360 nm which we identify as due to electron recombination with V_4 centers. The photon energies at the emission intensity peak are consistent with the known band gap and known energies of the V_3 and V_4 centers established by photoabsorption measurements. The behavior of the luminescence intensity as a function of temperature and dose is quite consistent with other more direct measurements of F-, V_3-, and V_4-center formation.

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