

Interaction of Slow Electrons With Insulating Crystals. 2. Comparison of Electron and Photon Absorption Coefficients for KCl and KBr†*

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The electron absorption coefficient for pure KCl and additively colored KCl and KBr was measured in the energy range from 0.2 to 12 ev. These data are compared with photon absorption measured in the same crystals in the energy range from 1.2 to 6.5 ev and with published optical and photoemission data above 6.5 ev. Certain imperfection interactions were found at corresponding photon and electron energies. The surface transition layer, even for pure KCl, was observed to contain F and V_3 centers. There was no evidence of direct electron-exciton interactions. The valence band of KCl was observed to be 8.6 ± 0.2 ev below the vacuum level; this agrees with Eby, Teegarden, and Dutton's measurements. Upon electron bombardment, an optical absorption near the first fundamental band was found to develop. Its characteristics do not coincide with any of the absorption bands previously reported in this energy region.

I. INTRODUCTION

SEVERAL attempts have been made to correlate the observed results of electron-insulating crystal interactions with the target's band structure. In an early study of low-energy electron reflection from evaporated films of KCl, Hilsch¹ found that a sharp change occurred in the reflection coefficient at an energy near the optically assigned band-gap width. More recently, Jacobs *et al.*² systematically investigated interactions between slow electrons and evaporated films of KCl and attempted to correlate inflections in the observed target current with various photon interactions which have been reported in the literature. Fridrikov and Goryacheva³ studied the secondary emission from cleaved alkali halide crystals for electrons impacting with energies greater than 3.5 ev. The results of these three studies are in apparent conflict. The present authors⁴ observed the absorption coefficient δ_a for 0.2- to 12-ev electrons on pure KCl and on additively colored KCl and KBr, and outlined probable causes for the discrepancies among the previous measurements.

Most investigators interpret the structure found in electron absorption or reflection coefficients as a function of energy, as electron interactions with the various crystal imperfections which have been observed optically. However, no previous investigation has compared the electron and photon absorption in the same target crystal, although correspondence has been frequently assumed. The results of direct measurements of photon and electron absorption for target crystals

cleaved adjacent to each other from the same parent crystal are discussed in this paper.

II. EXPERIMENTAL METHOD

The apparatus used and methods required for uniquely measuring the electron absorption coefficient have been previously described in detail: Briefly, the apparatus consists of an electron accelerator,⁵ target chamber,⁴ and vacuum crystal cleaver.⁴ The electron accelerator is capable of delivering a beam with a minimum energy dispersion corresponding to a temperature ranging from 750° to 1000°K in the energy range from 0.2 to 30 ev. The mean beam energy at the target chamber entrance aperture can be determined to within 0.03 ev. The target chamber (shown in Fig. 1) consists of a target holder with a hollow stem in which a heater and thermocouple can be placed; a 2π spherical collector for secondary and reflected electrons shielded from the target by a high-transparency grid; and a collecting electrode behind the target to measure the defocused beam. The crystal cleaver is attached to the back plate of the target chamber when required.

The experimental method and the precautions necessary to obtain unique data have been previously described in detail.⁴ It was found that effects due to trapping of electrons in deep and shallow traps could strongly perturb the data. Effects due to shallow trapping could be essentially removed by pulsing 3×10^{-13} amp beams 10 μ sec on and 15 μ sec off. Deep trapping was reflected as residual surface potential. Measurement of residual target potential showed that pure KCl after each bombardment retained a charge which could be removed by heating to 230°C for 45 to 60 min. The additively colored crystals did not retain a residual charge and thus were only occasionally heated as a precautionary measure.

The target crystals, $4 \times 4 \times 1$ mm, were cleaved from the same parent crystal of each material, i.e., pure KCl, additively colored KCl or KBr. These crystals were

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¹ R. Hilsch, *Z. Physik* **77**, 427 (1932).

² H. Jacobs, I. N. Greenberg, L. Goble, and A. Ramsa, *Phys. Rev.* **106**, 921 (1957).

³ S. A. Fridrikov and G. N. Goryacheva, *Izvest. Akad. Nauk S.S.S.R.* **22**, 486 (1958) [translation: *Bull. Acad. Sciences U.S.S.R.* **22**, 491 (1958)].

⁴ C. J. Cook and W. J. Fredericks, *J. Appl. Phys.* (to be published).

⁵ C. J. Cook, *Rev. Sci. Instr.* (to be published).

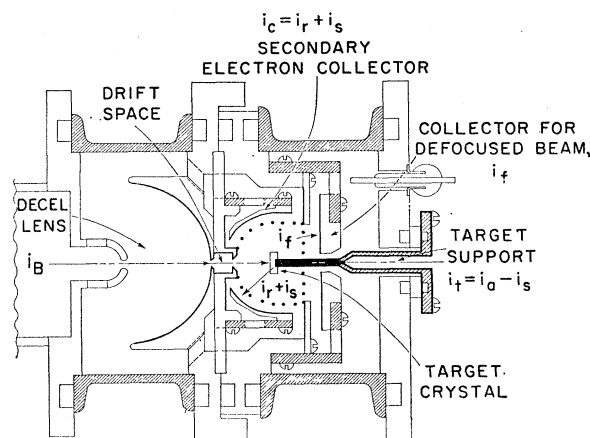


FIG. 1. Assembly drawing of the target chamber.

obtained from Professor A. B. Scott, Oregon State College, Corvallis, Oregon. After cementing (Emmerson and Cumings, Inc., Eccobond 56C or 60L conducting cements) the crystal to the target holder, the holder was placed in the cleaver. After evacuation the crystal was cleaved and the part remaining on the target holder was inserted into the target chamber—this operation also being performed under vacuum. The cleaver was then removed from the electron absorption apparatus. The free piece of crystal taken from the cleaver was used to obtain the photon absorption reported herein as the “before” data. After measurement of the electron absorption coefficient by methods previously described,⁴ the crystal was removed from the target holder and the “after” photon absorption curves were measured.

Optical absorption measurements were made with a Cary model 14 M spectrophotometer. All measurements reported were made in air against a standard aperture. The wavelength range used was from 1850 to 10 000 Å.

The electron absorption coefficient is obtained by an extrapolation technique. After the crystal's surface charge has been removed by heat cycling, the beam is

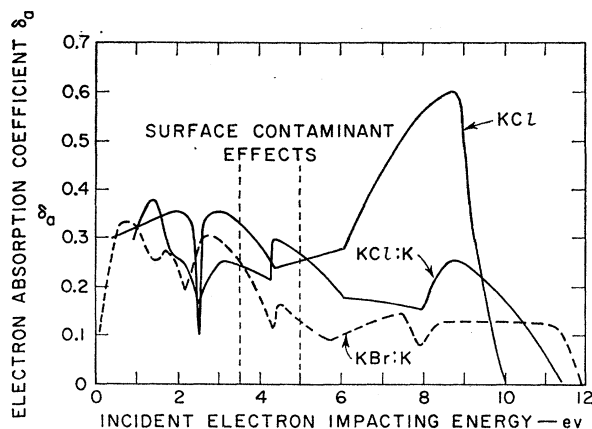


FIG. 2. Comparison of electron absorption coefficients for various alkali halides.

turned on and the target current i_t and secondary electron collector current i_c are measured as a function of beam bombardment time (Fig. 1). From these a time-dependent electron absorption coefficient δ_a'' can be defined as

$$\delta_a'' = i_t / (i_t + i_c), \quad (1)$$

provided that i_f , the beam current missing the target is negligible. By extrapolating δ_a'' to zero beam time, a unique value δ_a can be determined if all measurements are made with pulsed, low-intensity beams that satisfy the uniqueness requirements for this experiment. (These requirements are fully discussed elsewhere.⁴) From Fig. 1 it may be seen that Eq. (1) can be expressed as

$$\delta_a'' = (i_a - i_s) / (i_a + i_r),$$

where i_a is the charge influx to the crystal, i_s is the secondary electron current, and i_r is the reflected electron current.

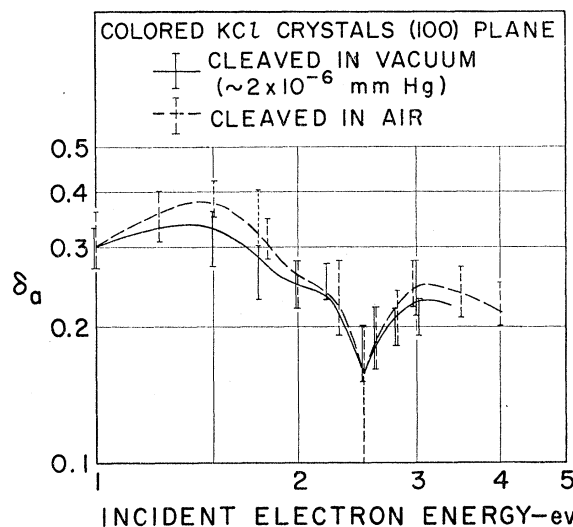


FIG. 3. Comparison of electron absorption coefficients for colored KCl cleaved in air and vacuum.

III. EXPERIMENTAL RESULTS

A. Electron Absorption

The electron absorption coefficients δ_a for pure KCl and additively colored KCl and KBr (KCl:K and KBr:K) have been determined⁴ and are compared in Fig. 2. The electron absorption coefficients for KCl, colored KCl, and colored KBr show remarkable self-consistency. Common features are observed for pure and colored KCl. δ_a for both pure and colored KCl has sharp negative inflections at 2.5 ev. (Inflection as used here refers to the intersection of two lines of differing slope.) Other common inflections occur at 6.15 ev and near 4.40 ev. δ_a for colored KCl exhibits additional structure at 8.0 ev and below 2.0 ev. A further difference between pure and colored crystals is the energy at which $\delta_a = 0$. For the colored KCl it is shifted toward higher energies.

The bulk F -center concentration was estimated from optical absorption measurements to be $6 \times 10^{17} \text{ cm}^{-3}$ in the colored KCl and about 10^{18} cm^{-3} in colored KBr.

All crystals studied exhibited one narrow energy region between 3 and 5 eV, where the electron absorption coefficient was not reproducible. This nonreproducibility has been attributed to surface contamination effects. However, the adjacent energy regions were independent of crystal cleaving conditions. For example, Fig. 3 shows a detailed comparison of δ_a between air- and vacuum-cleaved colored KCl crystals in the 0.5- to 3-eV region.

B. Photon Absorption

The electron and photon absorption coefficients representing data obtained from several pure KCl slabs cleaved adjacently from the same parent crystal are shown in Fig. 4. For reasons discussed later, the electron absorption coefficient has been displaced 0.3 eV toward

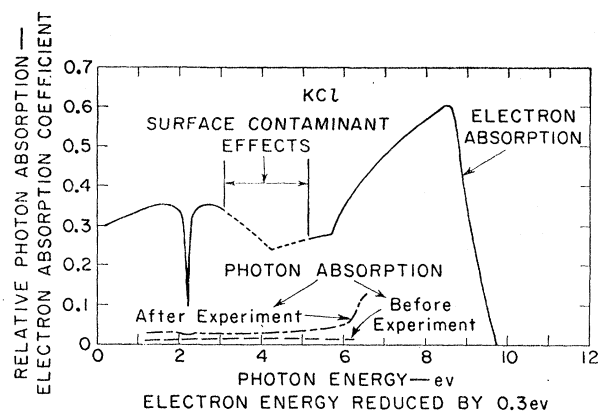


Fig. 4. Relative photon absorption and electron absorption coefficient for KCl as a function of energy and target history.

lower energies. It is of particular interest to note that the lack of structure in the pure KCl photon absorption coefficient before electron bombardment clearly demonstrates that these crystals are free of bulk impurities and imperfections which absorb in the 1850 to 10 000 Å region. After electron bombardment, however, a new band has developed in the KCl. Unfortunately, only the initial rise at 6.25 eV could be observed with the optical equipment available.

Figure 5 shows both the electron and photon absorption coefficients representing data obtained from several additively colored KCl slabs cleaved adjacently from the same parent crystal. The electron absorption coefficient has again been shifted by -0.3 eV to make the correspondence apparent between the electron and photon data. The photon absorption before electron bombardment shows only an F band and the lower energy bands usually associated with it. After electron bombardment the F band has decreased and a strong band at about 6.25 eV has developed.

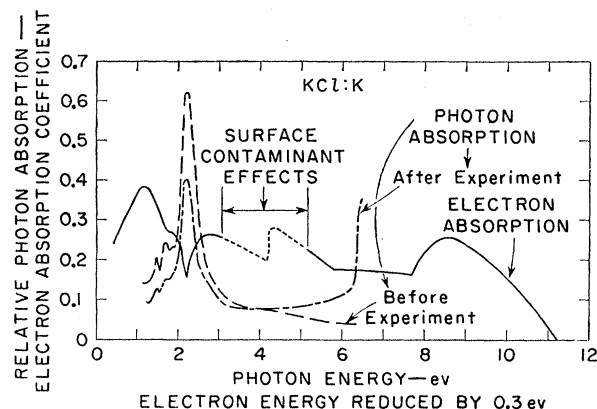


Fig. 5. Relative photon absorption and electron absorption coefficient for colored KCl as a function of energy and target history.

Similar data for the colored KBr are shown in Fig. 6. These electron absorption data have also been displaced by -0.3 eV. The colored KBr exhibits not only an F band but a strong band rising at 6.00 eV with a shoulder at 5.35 eV. Studies of the band edge at 6.00 eV, observed both before and after the electron absorption coefficient was determined, indicate that this band increases during electron bombardment.

IV. DISCUSSION

The similarity of structure between the photon and electron absorption coefficient as a function of the incident photon or electron energy is striking for the colored crystals. Table I gives the energies at which strong electron interactions (inflection points in δ_a) were observed in pure and colored KCl and compares them with energies of photon interactions. Where available equipment permitted direct optical observation on the crystal, these are given; otherwise the data were obtained from the reference cited. Table II lists the experimental results for colored KBr. The data presented in Tables I

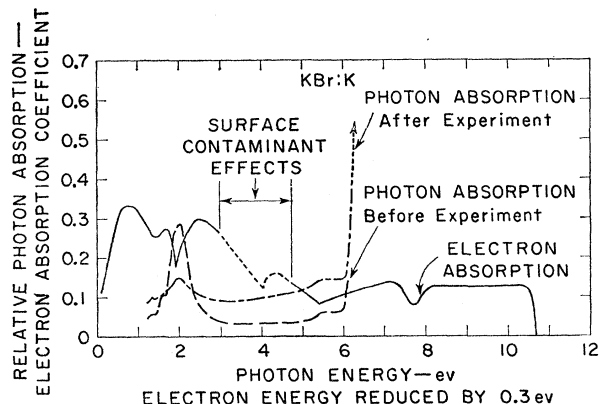


Fig. 6. Relative photon absorption and electron absorption coefficient for colored KBr as a function of energy and target history.

TABLE I. Electron and photon absorption in KCl.

Electron absorption band				Photon absorption band		
Observed energy (ev)		Observed energy (ev) less 0.3 ev		Observed energy (ev)		Center
Pure	Colored	Pure	Colored	Pure	Colored	
	~1.90		~1.60	None	1.5	<i>M</i>
2.50	2.50	2.20	2.20	None	1.7	<i>R₂</i>
				None	2.20	<i>F</i>
4.45	4.35	4.15	4.05	None	None	...
6.15	6.15	5.85	5.85	None	5.85 ^a	<i>V₃</i>
	7.90		7.60	<6.25 ^a	<6.25 ^a	...
				7.76 ¹⁰	7.76 ¹⁰	1st exciton
8.90	8.90	8.60	8.60	8.5 ¹⁰ , 9.44 ¹¹	8.5 ¹⁰ , 9.44 ¹⁷	<i>E_g</i>
				8.7 ^{16,b} , 8.3 ^{15,b}		<i>E_g</i> + <i>x</i>

^a Only after electron absorption measurement.^b From photoemission data.

and II suggest a correspondence between electron and photon interactions with certain crystal imperfections. The following discussion of this correspondence is based upon the assumption that a systematic experimental error is present in the data and that this error can be removed by shifting the energy scale -0.3 ev. The source of this assumed error will be discussed later.

The strongest inflection in the experimentally measured electron absorption coefficient in the colored crystals corresponds very closely to the energy at which the optical absorption band assigned to *F* center occurs. This energy correspondence was also found in both the colored KCl and KBr; however, structure was observed on the low-energy side of this inflection which was not completely resolved by these measurements. In colored KCl and colored KBr this structure occurs approximately at the *R*- and *M*-absorption band energies observed in these crystals. Thus, the strong inflection near 2.2 ev can be considered with some confidence to be due to electron-*F*-center interactions.

The inflection point at about 4.5 ev occurs in the energy region where the data were sensitive to crystal history. The heats of formation of various simple potassium compounds such as KCl, KBr, K₂O, and KOH are all in the range from 3.5 to 5 ev; however, chemical dissociation should not give rise to the sharp inflections observed,⁶ but should occur over a range of energies. The conclusion that this surface-sensitive inflection is not due to actual chemical dissociation is supported by Wargo.⁷ He found for the alkaline earth oxides that electron crystal interactions in this energy range resulted in the evolution of absorbed gases. Without experiments which uniquely associate this inflection with definite surface contaminants or imperfections sensitive to surface treatment of the crystal, no assignment can be made.

Another major inflection occurs at 5.85 and 5.45 ev

in colored KCl and KBr, respectively, after the -0.3 -ev scale correction has been made. These agree with the optical energies reported for *V₃* centers in KCl (5.85 ev) and KBr (5.35 ev). There is a weak absorption band observed in colored KBr at 5.35 ev both before and after electron bombardment. However, in colored KCl, a broad absorption band about 5.85 ev appears only after electron bombardment.

At 7.90 ev an inflection was found in the colored crystals that is apparently independent of the host lattice and depends on the presence of nonstoichiometric potassium. An optical lattice absorption occurs in KCl at an energy close to this inflection and is usually attributed to exciton formation. However, for pure KCl there is no indication in the data of exciton formation; furthermore, if it were due to exciton-nonstoichiometric potassium interactions, the inflection in KBr should be at about 6.7 ev. No definite correspondence was found between this inflection and known optical absorption bands.

In pure KCl, inflections were observed at 2.20, 4.15, and 5.85 ev (after the -0.3 -ev scale shift). The inflection at 4.15 ev lies in the energy region sensitive to the history of the crystal surface. No discussion other than that given for the colored crystals would be applicable here, and the nature of these interactions must await further research. However, the 2.20-ev and 5.85-ev inflections agree energetically with the *F*- and *V₃*-center interactions found in the colored crystals. The 2.20-ev inflection has no low-energy structure, is symmetrical, and has a much narrower "band" width than the colored crystal. This structure is suggestive of a classical thin-film interaction.

The optical measurement methods used could not detect a high *F*-center concentration if it were present only in a sufficiently thin surface layer. For example, under the most favorable conditions a surface layer 300-

TABLE II. Electron and photon absorption in colored KBr.

Electron absorption band		Photon absorption band	
Observed energy (ev)	Observed energy (ev) less 0.3 ev	Observed energy (ev)	Center
1.7±0.2	1.4±0.2	1.4	<i>M</i>
		1.6	<i>R₂</i>
2.30	2.00	2.05	<i>F</i>
4.25	3.95	None	...
5.75	5.45	5.35 ^a	<i>V₃</i>
		<6.25 ^a	...
7.90	7.60		
		6.77 ¹⁰	1st exciton
8.3–11.2	8.00–10.9	7.8 ¹⁰ , 8.5 ^a	<i>E_g</i>
		8.1 ^{16,b}	<i>E_g</i> + <i>x</i>

^a Apparent increase after electron absorption measurement.^b From photoemission data.⁶ D. A. Wright and J. Woods, Proc. Phys. Soc. (London) **66**, 1073 (1953).⁷ P. Wargo and W. G. Shepherd, Phys. Rev. **106**, 696 (1957).

lattice-constants thick with an F -center concentration of 10^{19} -centers cm^{-3} , the maximum density of F centers that can be produced by irradiation,⁸ would be barely detectable. If a crystal is exposed to light in its fundamental absorption band, a layer of F centers no thicker than about 10^{-6} cm or about 16-lattice-constants is produced⁸ and, of course, could not be detected by the optical equipment used. Thus it is not surprising that pure KCl exhibits no photon absorption spectra characteristic of the various centers detected in the slow electron absorption studies where interactions occur dominantly in the surface layers. The electron-crystal interactions at F - and V_3 -center energies show that in pure KCl a relatively high concentration of imperfections exist near the geometrical surface, i.e., the thin, bulk-surface transition region.

The maximum observed in δ_a at 8.6 ev (after the 0.3-ev scale shift) in both pure and colored KCl is of particular interest. The removal of an electron from the valence band of an insulating crystal to the vacuum level requires energy equal to the energy difference between the top of the valence band and the bottom of empty band E_g plus χ the electron affinity.⁹ An incident electron gains energy equal to χ on entering the crystal. Thus, the onset of secondary emission would be expected to occur when the incident electron's energy is equal to E_g and, after exceeding E_g , the electron absorption coefficient should plunge catastrophically through zero. It will become negative when the secondary emission current exceeds the charge influx to the target crystal, i.e., when $i_s > i_a$. Based on these considerations, the data obtained from electron absorption experiments in KCl are consistent with a forbidden energy gap of 8.6 ev.

This measurement of E_g is in excellent agreement with the value 8.5 ev reported in the recent ultraviolet absorption studies by Eby, Teegarden, and Dutton.¹⁰ The results of both of these studies are more consistent with the photoemission studies which measure $E_g + \chi$, than they are with the previously accepted value 9.44 ev.¹¹ Vasek and Anderson¹² and Turner¹³ found the bottom of the conduction band in NaCl lies within 0.1 ev of the vacuum level by determining the energy required for internal photoemission from a metal into the insulating crystal.¹⁴ Thus, the optical and electron absorption measurements should differ from photoemission measurements only by χ , which is small. Based on extensive measurements of external photoemission yield and the energy distribution of emitted electrons, Taylor and

Hartman¹⁵ find the valence band to lie 8.3 ev below the vacuum level. Taft and Philipp¹⁶ report a value of 8.7 ev from careful measurements of photoelectric quantum efficiency. For KCl, Eby *et al.*¹⁰ report $\chi = 0.2$ ev using Taft and Philipp's¹⁶ photoemission data; however, if Taylor and Hartman's¹⁵ data had been used, χ would be -0.2 ev. While discrepancies exist between photoemission and the optical or electron impacting measurements, they are only of the order of 0.4 ev. Only one other pertinent measurement of band gap by electron bombardment technique has been reported. Jacobs *et al.*² assumed an electron affinity of 0.3 ev and obtained a band gap of 9.5 ev from electron bombardment data on evaporated KCl films. The differences between Jacobs *et al.* and the present studies have been discussed by the present authors.⁴

In colored KBr, the electron absorption coefficient data are severely perturbed in the region of the band edge by the 7.9-ev interaction characteristic of additively colored crystals. Eby, Teegarden, and Dutton¹⁰ report the band gap of KBr to be 7.8 ev. The energy difference between the valence band and the vacuum level is 8.1 ev from the photoemission experiments of Taft and Philipp.¹⁶ The electron affinity is then 0.3 ev from these measurements. At present the electron absorption data on KBr do not allow an unequivocal estimate of the band gap energy, for there is no clearly defined maxima. This must await the development of experimental techniques suitable for studying pure KBr.

Both colored KBr and KCl exhibit severe electron-defect trapping¹⁷ of the secondaries. This is evident from the decrease in the slope of the characteristic plunge of δ_a through zero after the onset of true secondary emission of colored KCl compared to pure KCl. In the colored KBr, this trapping of secondary electrons may be responsible for the plateau from 8.3 to 11.2 ev.

During the measurement of δ_a both pure and colored KCl developed a new optical absorption band which rises at about 6.25 ev, near the short wavelength limit of the Cary spectrophotometer. A similar band, which rises about 6.0 ev, was already present in colored KBr before electron bombardment and became enhanced during the experiment. The origin of these bands is obscure at present; the only band stable at room temperature that has been reported in this energy region is the β band. Measurements have not yet been made to correlate the growth rate of these bands with the number of incident electrons, their energy, or other experimental parameters; however, some experimental facts can be reported. The average KCl crystal had been heated to 230°C for 1 hr about 20 times; the colored crystals were similarly heated but only 4 or 5 times. Samples which had been attached to the target holder

⁸ F. Seitz, *Revs. Modern Phys.* **26**, 87 (1954).

⁹ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940), p. 400.

¹⁰ J. E. Eby, K. J. Teegarden, and D. B. Dutton, *Phys. Rev.* **116**, 1099 (1959).

¹¹ H. Dorendorf and H. Pick, *Z. Physik* **128**, 106 (1950).

¹² L. S. Vasek and J. M. Anderson, *Proc. Phys. Soc. (London)* **73**, 733 (1959).

¹³ W. S. Turner, *Phys. Rev.* **101**, 1653 (1956).

¹⁴ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1950), p. 97.

¹⁵ J. W. Taylor and D. L. Hartman, *Phys. Rev.* **113**, 1421 (1959).

¹⁶ E. A. Taft and H. R. Philipp, *J. Phys. Chem. Solids* **3**, 1 (1959).

¹⁷ A. J. Dekker, *Physica* **21**, 29 (1954).

with either graphite or silver-based conductive cement had the same new band present. This new band was also observed in crystals which had been cleaved to remove the side glued to the target holder before the optical measurement. Thus, this band is not due to the cementing of the crystal, but represents a change due to the slow electron bombardment. All crystals were bombarded with between 10^{10} and 10^{11} low-energy electrons. If all of the electrons incident on the crystal formed a center responsible for optical absorption in this band near 6 eV, too few centers would be present at termination of the experiment to be detected by optical measurements. If the absorbing centers were produced by bleaching the F centers, the band should not appear in pure KCl. At present an adequate interpretation cannot be given for this band.

In the foregoing discussion, the 0.3-eV shift toward lower energy of the electron absorption data necessary to bring them into agreement with optical absorption data was treated as a simple energy scale correction. However, this correction exceeds the experimentally established error in the measurement of the mean beam energy by 0.1 eV⁵ and thus could provide information about the target crystals. The electron-crystal interactions are detected by sharp excursions of δ_a and they arise when a marked change in electron scattering or secondary emission occurs. It is assumed that the incident electrons have interacted with an imperfection or that new electrons have been ejected from the filled band. When an electron enters an insulating crystal, it gains or loses energy^{9,14} equal to χ , the electron affinity. If the electron affinity is positive, then the energy ϵ_i of the incident electron is increased to $\epsilon_i + \chi$. In this case the interactions would occur at energies less than the corresponding optical interaction and would be detected as an increase in δ_a . If the electron affinity is negative, the energy ϵ_i of the incident electron is decreased to $\epsilon_i - \chi$. The energy at which the electron interaction occurs would then exceed that of the energy required for the corresponding photon interaction and would be detected as a scattering event. The latter case is observed in these experiments, i.e., $\chi = -0.3$ eV. While this result agrees well with that obtained from comparing Taylor

and Hartman's¹⁵ photoelectric measurement to the optical absorption measurements of Eby *et al.*,¹⁰ it represents an apparent electron affinity for crystal surfaces prepared under these experimental conditions and measured with the crystal mounted in the manner described. Many explanations can be proposed to account for the observed "apparent electron affinity." Any model which will uniformly decelerate the incident electrons by 0.3 eV would be satisfactory; for example, it could be attributed to a surface dipole layer due to absorbed gases, to contact potentials, etc. The evidence on hand supporting any single source is highly circumstantial, and further research must be performed to substantiate any one of them.

V. CONCLUSIONS

These experiments, while creating many new questions, do clearly show that an energy correspondence exists between electron and photon interactions with crystal imperfections. Within experimental error, the 8.6 ± 0.2 eV KCl band gap found in this experiment is in agreement with optical absorption and photoemission measurement. The incident electron undergoes similar interactions at 2.2 eV in clear and colored crystals. From a consideration of the energy of interaction, variation of linewidth, and the observation of associated low-energy structure, the 2.2-eV interaction is ascribed to F centers. If this assignment is correct, a thin layer of F centers must exist near the surface of even a pure KCl crystal. Similarly, a thin layer of V_3 centers must exist in the same region.

The need for further research in low-energy electron-solid interactions is obvious from the surface treatment sensitive inflection at 4.15 eV and the 7.9-eV inflection found only in colored crystals which is apparently independent of the host crystal. Further, the new optical band which is produced by slow electron bombardment must be characterized.

ACKNOWLEDGMENT

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