Photoelectron Emission from Solid Sodides*

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Emission of photoelectrons from various sodide salts has been observed over the energy range 3.5–1.5 eV [350–800 nm]. The photoionization action spectrum shows two peaks at 3.4 and 2.0 eV. The quantum yield for emission is low (10^{-4} or smaller), indicating a short escape depth of the "hot" electrons which are effectively retrapped. The shape of the higher-energy peak is relatively independent of temperature and is attributed to emission from the sodium anion, Na^-. By contrast, the low-energy emission is markedly broadened and increases more rapidly in amplitude than the second peak when the temperature is increased. This peak, whose shape and amplitude depend on the cation, the complexing agent used, and the age of the film, is attributed to emission of electrons trapped at lattice defect sites. Because the maximum photocurrent occurs at wavelengths at which Na^- has its maximum absorption, we suggest a mechanism in which energy transfer from an excited sodium anion to a trapped electron results in electron emission. © 1984 Academic Press, Inc.

Introduction

Photoelectron emission (PEE) from a semiconductor or insulator can provide insight into the electronic band structure. The information gained is in many respects comparable to that derived from the optical absorption spectrum; PEE is less ambiguous since not all possible transitions, but only those with final states with an energy higher than the vacuum level (V_0), contribute to the observed spectrum (1–3).

Up to about 1960, it was generally assumed that photoelectron emission was exclusively a surface process. Then, following the work of Meyer and Thomas (4), which showed that PEE from alkali metals

can originate from depths several hundred Ångstroms below the surface, volume production of photoelectrons became the favored picture. Today, it is evident that both volume and surface processes influence photoelectron emission (5). Nevertheless, bulk properties can be probed quite unambiguously by PEE and the related technique of photoelectron spectroscopy and the method became a favorite tool for the examination of band structures in solids. Spicer (6) proposed a semiclassical picture in which the electron emission process is divided into three steps.

(i) Ionization of an atom, ion, or molecule in the bulk of the solid and generation of an energy-rich electron–hole pair.

(ii) Motion of the electron toward the solid–vacuum interface. During this process, the electron can lose (or gain) energy

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due to electron–phonon or electron–electron scattering and—for electrons with sufficient kinetic energy—plasmon excitation.

(iii) Escape of those electrons with sufficient kinetic energy *normal to the surface* over the surface barrier; some of the energy-rich electrons are reflected at the surface barrier. The reflection coefficient $R(E)$ is a function of the electron energy; if one makes the plausible assumption that $R(E)$ is only slowly varying over the energy range of interest in our work the number of escaping electrons is directly proportional to the number of generated excited electrons in the solid and therefore to the joint density of states (*1, 7*).

In the present case, which deals with electrons with comparatively low energy (~1 eV), all effects except electron–phonon scattering can be neglected. In this case the exchanged energy is so low (~20–30 meV) that the redistribution of energy can be neglected in first approximation. A more severe problem is posed by impurity scattering and the variation of the work function in polycrystalline samples (*8*). These effects have the greatest influence on the low-energy tail of the photoemission spectrum. At excitation energies >1.5 eV the effects are small and useful information can be extracted from photoionization quantum yields.

Besides the information on optical transitions contained in the photoionization action spectra, an examination of the quantum yield near threshold permits not only the determination of the work function but also gives information on the nature of the transition. Fowler (*9*) treated the problem of photoemission from metals on the basis of the quantum theory of electrons in metals. He showed that one expects a dependence of the quantum yield, γ, on the energy of the exciting light according to

$$\gamma \alpha (E - \phi)^2 \qquad (1)$$

where ϕ is the work function. Kane (*10*)

extended the theory to cover photoelectron emission from semiconductors. He took into consideration problems posed by band-bending as well as the existence of a space charge; the results showed that γ is a function of $(E - \phi)^n$ where n is a multiple of $\frac{1}{2}$. The n is sensitive to the nature of the absorption process as well as the predominant scattering processes. A direct optical transition with conservation of momentum results in the highest threshold and gives $n = 1$.

Dye and co-workers (*11–14*) have shown that solid salts in which the anions are *alkali metal anions* (alkalides) can be obtained in crystalline form from solutions of the appropriate alkali metal(s) and macrocyclic complexing agents in suitable solvents. The complexing agents used to synthesize alkalides are macrocyclic polyethers (crown ethers) and macrobicyclic diamines (cryptands). Except for sodides, alkalides are usually highly unstable compounds and decompose at temperatures above $-20°C$. Some sodides on the other hand are exceptionally stable. For example, $Rb^+(15C5)_2 \cdot Na^-$ melts at 75°C prior to decomposition (*15*). These compounds therefore are excellent candidates for more intensive investigation into their structural and electronic properties.

Previous studies (*16–19*) examined electron detachment from isolated alkali metal anions in a molecular beam. These workers accurately determined the electron affinities of the alkali metal atoms as well as the possible channels for autoionization and electron loss of the excited alkali metal anions. Delahay and co-workers (*8, 20–22*) measured PEE from solutions of sodium in hexamethylphosphoramide. The species responsible for photoemission in this case are the solvated electron and the solvated sodium anion. In this paper we present the first measurements on photoemission from sodium anions and electrons in the rigid matrix of a sodide crystal.

Experimental

The sodide salts were prepared as described elsewhere (23, 24). Photocathodes were formed by dissolving several milligrams of the appropriate sodide salt in a few drops of methylamine followed by solvent evaporation. With care, a uniformly coated cathode results from this process. All handling of the air- and moisture-sensitive sodides took place in the inert atmosphere of a glove bag or in vacuo.

The phototube used in this study is shown in Fig. 1. It consists of two parts and is made entirely from Pyrex. The top has a window and an electrical feed-through to the collector which was constructed from a piece of stainless-steel tubing. In the lower part is the cathode, a platinum disk that is in thermal contact with the bottom of the vessel. Platinum has a sufficiently high work function that PEE from the metal is negligible compared to the emission from the coating. The necessity to prepare films by solvent evaporation, the high reactivity of sodide salts, and the need to keep the temperature low prevented the use of more conventional designs of photoemission cells. This made it impossible, for example, to study energy distribution curves. The vacuum in the cell is limited by the vapor

pressure of the sodide salt; continuous pumping with a small ion pump (Varian Associates, Model 202-01, 1 l s^{-1}) maintained a vacuum of better than 10^{-4} Torr. Experiments showed that neither the magnetic field nor the ion current from the pump interfered with the measurement of PEE-spectra. The lower part of the cell was immersed in a Dewar flask which contained cooled isopropanol, and spectra were taken during warm-up. The temperature was monitored with a copper–constantan thermocouple mounted on the outside of the cell next to the photocathode. During the time it took to record a spectrum, the temperature increased typically by 2–3°C. The distance between emitter and collector was fixed at 5 mm.

The optical system for the exciting light consisted of a 75-W high-pressure xenon lamp (Oriel) with a quartz collimator, a Bausch & Lomb high-intensity grating monochromator and a 90° mirror to illuminate the photocell through the top. The spectral bandwidth was ~10 nm. The use of glass lenses limited the transmitted radiation to $\lambda > 300$ nm so that photoemission from the anode materials was not a problem. For wavelengths >600 nm, a cutoff filter (Pyrex No. 378) was inserted in the beam.

The light flux into the cell was measured at various wavelengths by replacing the cell with a thermopile detector with flat response (Scientech Model 362). A continuous curve was obtained by using either a Si-photodiode (UDT-6DP) or a photomultiplier (Hamamatsu R585). The measured photocurrents, after correction for the wavelength dependence of detector sensitivity, were normalized to the values obtained with the thermopile detector. The accuracy of the quantum flux determination is ≈ ±20%. Baron et al. (20) discuss the possible errors introduced by stray light through the monochromator. Because we limit ourselves to the wavelength range
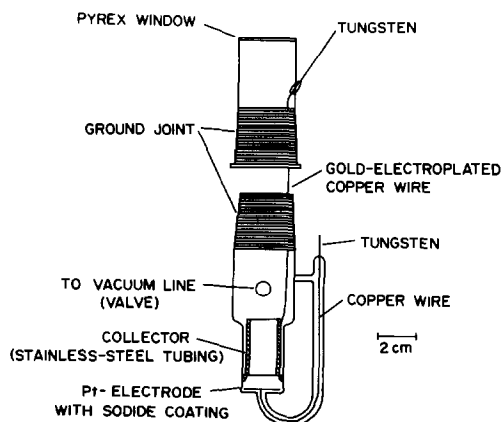

FIG. 1. Cell used to study photoemission from sodides.

350–800 nm where the photocurrent changes by only a factor of 1000, serious errors are not expected from this source.

The cell was mounted in a shielded enclosure. We found it necessary also to ground nearby optical components such as mirror mounts and lens holders. All cables to and from the cell were rigidly fixed to avoid triboelectric currents. A dc voltage, typically 50 V, was applied between emitter and collector. Photocurrents were measured point by point with a Keithley Model 417 picoammeter as the preamplifier and a Fluke Model 8000 A voltmeter for digital readout.

If the dark current was small and relatively constant, it could be compensated for with the picoammeter. Otherwise, readings with the light path open and blocked were taken and the difference was used as the value for the photocurrent. The sensitivity of the setup was about 0.1 to 0.01 pA. In some experiments the light beam was chopped at 170 Hz and the signal from the preamplifier was fed into a PAR Model 126 lock-in amplifier. At this high chopper frequency, only a comparatively low gain could be used in the picoammeter. Because of this and stray capacitance effects, the overall sensitivity was not markedly improved by the use of lock-in detection. However, modulation effectively eliminated all dark currents, resulting, e.g., from surface conductivity of the glass, which sometimes were bothersome.

Results and Discussion

The photoemission quantum yields from polycrystalline films of four different alkalides were measured as a function of the energy of the exciting light. The samples were $Na^+C222 \cdot Na^-$, which has a rigid structure with the cation encaged inside the cryptand molecule, $K^+18C6 \cdot Na^-$, where cation–electron interaction has been observed by EPR (24), and $Rb^+(15C5)_2 \cdot Na^-$ and $K^+(15C5)_2 \cdot Na^-$ which have sandwiched cations in a rather "soft" organic matrix.

Previous measurements of the resistivity showed that all these compounds are semiconductors or insulators with band gaps between 1 and 2.4 eV and conductivities $<10^{-6}$ ohm^{-1} cm^{-1} at 0°C (13, 25). The absorption spectrum of all these compounds is dominated by a broad, asymmetrical band at 1.80 to 1.95 eV (26–29). The photoemission spectra of these four compounds are surprisingly similar (Figs. 2–5). One always finds a peak at 370 nm and a second peak or shoulder at 600–650 nm. The absolute quantum yields on the other hand vary from $\sim5 \times 10^{-6}$ for $Na^+C222 \cdot Na^-$ to 2–3 $\times 10^{-4}$ for the other compounds.

The signal intensity shows a strong temperature dependence at all wavelengths. Generally, no photoresponse was found at liquid-N_2 temperatures. Measurements at
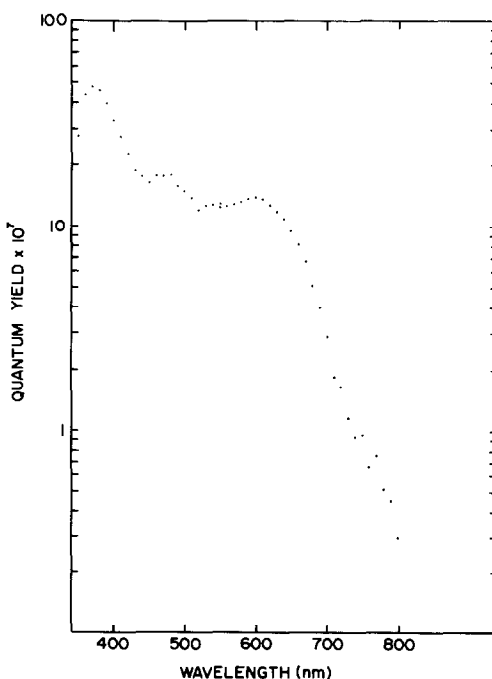

FIG. 2. Photoemission quantum yield versus wavelength for $Na^+(C222) \cdot Na^-$ at 298 K.
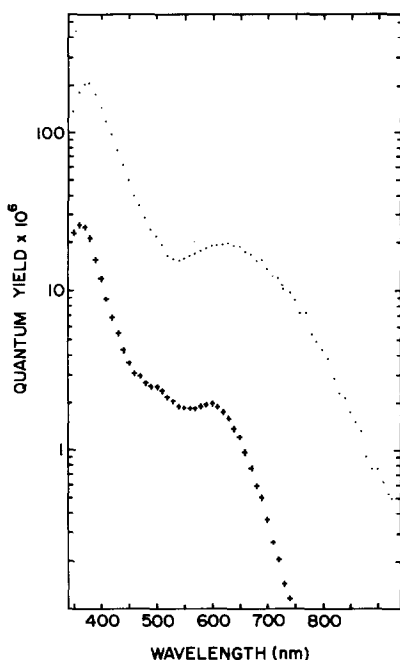
FIG. 3. Photoemission quantum yield versus wavelength for $K^+(18C6) \cdot Na^-$ at 289 K (upper curve) and at 231 K (lower curve).

−78°C were only occasionally possible. The simplest explanation is that the high resistivity of the film leads to slow charge neutralization at the surface. This seems to be the case with $Na^+C222 \cdot Na^-$, where the photocurrent increases almost linearly with the applied bias for fields >40 V/cm (Fig. 6). However, two effects argue against this interpretation. First, the currents observed in this work were so low that the voltage drop over a sample of ~1 μ thickness, calculated from the dc-conductivity value, is small compared to the bias voltage. Therefore, the buildup of a significant space charge within the solid is unlikely. Second, the photocurrent is proportional to the light intensity and therefore not limited by the bulk resistivity (if we exclude the possibility of an enhanced conductivity under illumination).

The effect of a space charge at the film–vacuum interface can be seen in these sam-

ples, which showed a field dependence that followed Schottky's theory (30)

$$i = i_0 \exp\left\{\frac{e_0^{3/2}E^{1/2}}{RT}\right\} \qquad (2)$$

where i_0 is the current in the absence of an external field. This equation was derived for thermionic emission but describes also the field dependence of a photocurrent. For small fields—as used in this work—the exponential can be linearized

$$i \simeq i_0(1 + C\sqrt{E}) \qquad (3)$$

which is the observed form of the field dependence at bias voltages greater than several volts (Fig. 7). The Schottky theory cannot explain the rapid decrease in photocurrent as the field approaches zero. The most plausible explanation for this behavior lies in the difference in work function between the steel collector electrode ($\phi \sim 4.5$ eV) and the sodide covered cath-
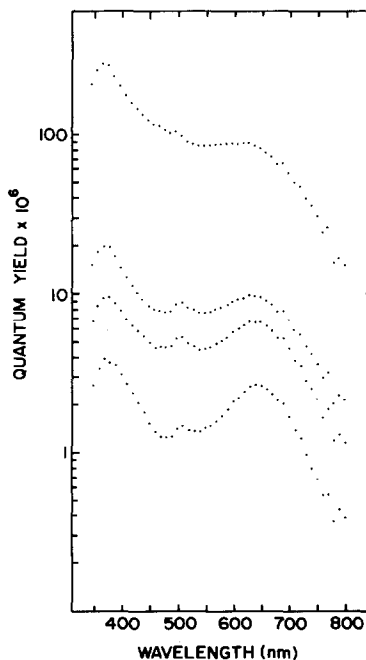

FIG. 4. Photoemission quantum yield versus wavelength for a fresh film of $Rb^+(15C5)_2 \cdot Na^-$. From top to bottom the temperatures are 277, 255, 245, 220 K.
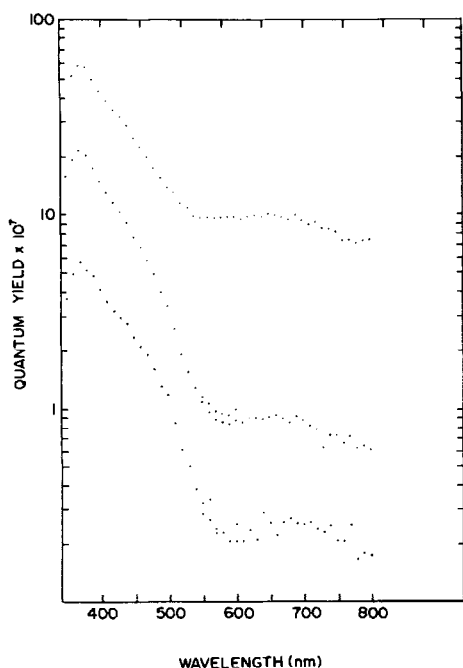
FIG. 5. Photoemission quantum yield versus wavelength of an "aged" film of $Rb^+(15C5)_2 \cdot Na^-$. From top to bottom the temperatures are 254, 248, 240 K.
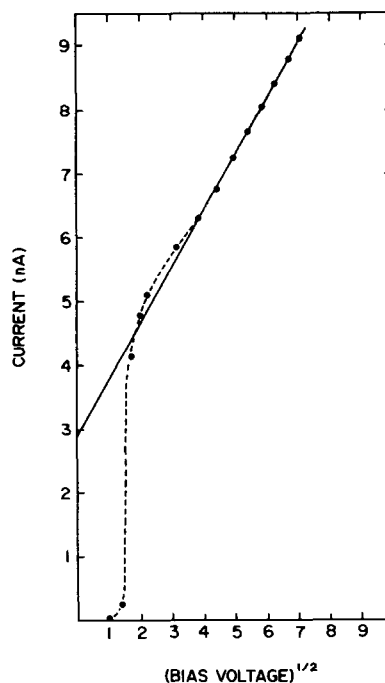

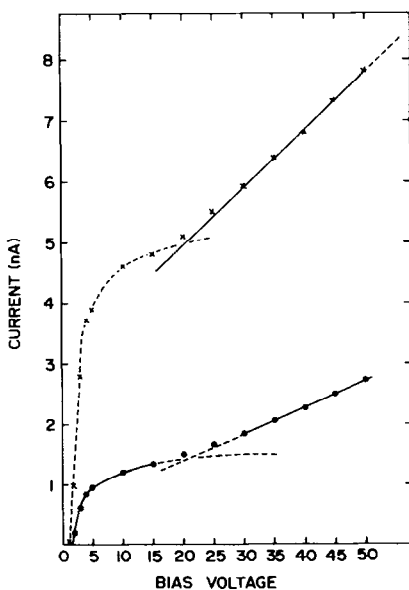FIG. 7. Photocurrent at 600 nm versus the square root of the bias voltage for a film of $Rb^+(15C5)_2 \cdot Na^-$ at 288 K.

FIG. 6. Photocurrent versus bias voltage for a film of $Na^+C222 \cdot Na^-$ at ambient temperatures. The lower curve corresponds to a lower light intensity.

ode ($\phi < 1.5$ eV). This leads to a contact potential difference so that the cathode in equilibrium is positive by ~ 3 V with respect to the anode. This potential difference has to be compensated by the external field in order to make a current flow. The onset of this current is not sharp, partly because, at the exciting wavelength, electrons with kinetic energies up to 1.5 eV are produced from the two photoemitters, e_t^- and Na^-, and partly because field inhomogeneities would tend to smear out a sharp step.

The peak at high energy is similar for all sodide samples studied and shows less temperature dependence than the low-energy peak. The maximum is found at ~ 3.4 eV.

Some samples show little photoresponse at longer wavelengths and permit extrapolation to the photoionization threshold with reasonable accuracy. For example, an "aged" sample of $Rb^+(15C5)_2Na^-$, has, at

600 nm, only 5% of the quantum yield found at the maximum near 370 nm. Over a range of ~0.8 eV above threshold a linear relationship between the quantum yield γ and $(h\nu - \phi)$ holds (Fig. 8). According to Kane (10) this implies a direct optical transition with conservation of momentum and escape of the electron without scattering—a surprising result considering the crude method used to prepare the films. This gives a value of 2.35 eV for the direct photoionization threshold. The extrapolation is less reliable in the case of $Na^+C222 \cdot Na^-$ and $K^+(15C5)_2Na^-$ but leads to similar values within the error limits of ± 0.1 eV. Only in the case of $K^+18C6 \cdot Na^-$ did the Na^- photoemission peak broaden with increasing temperature. An extrapolation to $i = 0$ is not very reliable because, due to the second peak at lower energy, only values far from threshold are useful; but it appears that the threshold energy decreases from
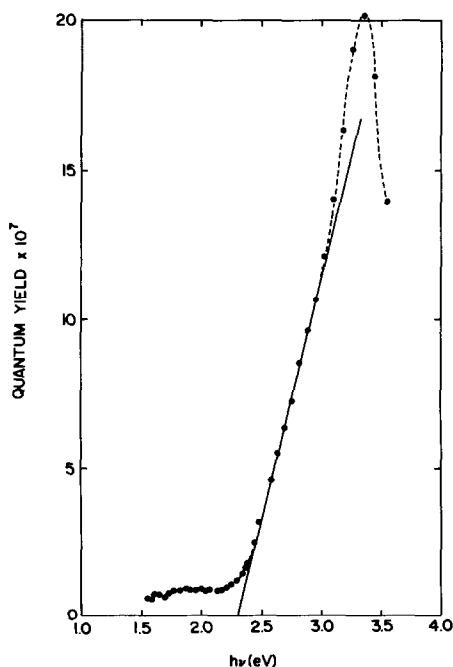

FIG. 8. Quantum yield versus photon energy for an "aged" film of $Rb^+(15C5)_2 \cdot Na^-$ at 248 K.

2.35 eV at $-42.5°C$ to 2.05 eV at $+16°C$. A lower photoionization threshold would be consistent with the lower band gap (1.02 eV) and red shift in the absorption spectrum (by .21 eV) of this compound compared to $Na^+C222 \cdot Na^-$ as found by Tinkham (24); on the other hand, no marked temperature dependence of the spectral shape or peak position was found (24).

The maximum in the quantum yield at higher energies is real and not an artifact caused by errors in the light flux determination. The photoionization peak is very similar to that observed by Delahay (20–22) in solution, but it is shifted by 0.35 eV to the blue in the solid compared to the solution. Delahay assigned this high-energy peak to photoemission from Na^-. The second photoemission peak at lower energies appears at wavelengths near the optical absorption peak of Na^-. It increases and broadens considerably with increasing temperature and is very pronounced in freshly prepared films, but reduced in intensity in "aged" films (after 24 to 36 hr). We conclude that the species responsible for this peak cannot be Na^-. The proposed energy band structure requires that, if this band were also attributed to Na^-, the energy of the vacuum level V_0 would have to lie well below the bottom of the conduction band—a situation which is clearly impossible. We therefore must assume that trapped electrons ("F-centers") are the source of photoemission at long wavelengths. The concentration of trapped electrons is probably much higher in freshly prepared films than in samples which have had time to anneal. Also, in $Na^+C222 \cdot Na^-$, where electron microscopy showed that even films formed by rapid solvent evaporation are exclusively crystalline, only a weak photoemission is observed at 600 nm, whereas compounds with a "softer" structure such as $K^+18C6 \cdot Na^-$ or the sandwich complexes are more likely to posess a higher degree of disorder

and therefore to contain a higher concentration of defect electrons. In addition, the latter sodides have dc powder conductivities which appear to be dominated by trapped electrons whereas $Na^+C222 \cdot Na^-$ behaves as an intrinsic semiconductor (13).

Again we find that the quantum yield decreases linearly to a threshold with decreasing photon energy so that a direct process appears to be responsible for the emission (Fig. 9). Considering the low concentration of trapped electrons (EPR and static susceptibility measurements show $\ll 1\%$ free spins), a high quantum yield would be necessary to explain the observed photocurrents. It also seems likely that the coincidence of the optical absorption peak of Na^- and the electron emission peak is not accidental. The following model would explain both of these phenomena. A light quantum has a very high probability of exciting a sodium anion when it passes through the sodide film. The resulting excited Na^{-*} can
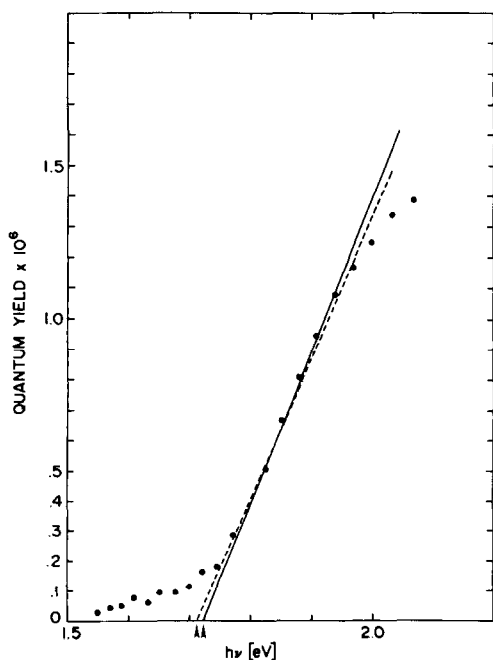
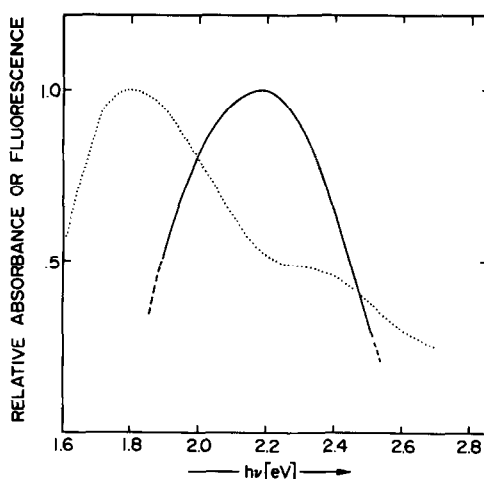

FIG. 10. Relative absorption (dotted line) and emission (solid line) spectra of a single crystal of $Na^+C222 \cdot Na^-$ at ambient temperatures. Excitation was at 2.54 eV with an argon-ion laser.

fall back into its ground state either by emission of a light quantum (fluorescence was recently observed in our laboratory, see Fig. 10) or by emission of phonons. Alternatively, it might transfer its energy to a trapped electron according to

$$e_t^- + Na^{-*} \rightarrow Na^- + e_{qf}^- \qquad (4)$$
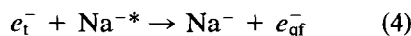
in which e_{qf}^- represents a quasi-free electron. The temperature-dependent broadening of the e_t^- emission peak observed for $K^+18C6 \cdot Na^-$ (Fig. 11) would then result from a broader distribution of trap depths with increasing softening of the lattice.

Recently, we also observed photoluminescence from $Na^+C222 \cdot Na^-$ single crystals after excitation with an Ar^+ ion laser. The photoluminescence spectrum, together with the absorption spectrum, is shown in Fig. 10. The emission is a nearly symmetrical band, centered at 2.2 eV. Since the emission appears on the high-energy side of the main absorption peak, we must conclude that this excitation does not lead to a photoluminescing state. Rather the shoulder at 2.3 eV, attributed to a bound-contin-
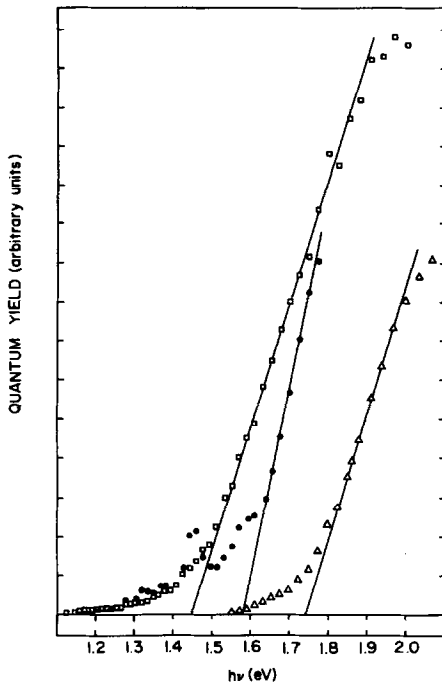

FIG. 9. Quantum yield versus photon energy for a film of $Na^+C222 \cdot Na^-$ at 298 K.

FIG. 11. Quantum yield versus photon energy for the low-energy photoemission peak of $K^+18C6 \cdot Na^-$ at 288 K (squares), 262 K (solid circles), and 231 K (triangles).
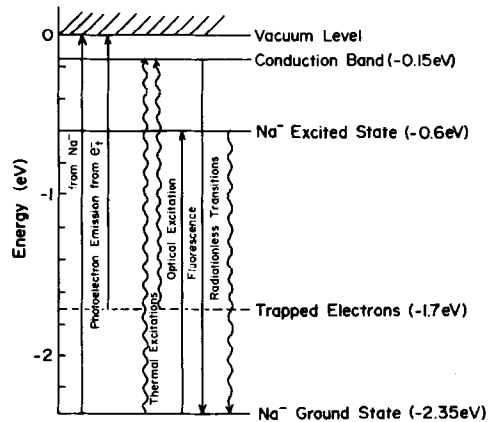

FIG. 12. Proposed energy level scheme for crystalline $Na^+222 \cdot Na^-$ which contains small concentrations of trapped electrons (F-centers).

uum transition, appears to be connected with the photoluminescing excited state.

With the combined information from the absorption spectrum, the dc-conductivity, the photoemission spectrum and the photoluminescence we can draw the following simplified energy diagram for $Na^+C222 \cdot Na^-$ (Fig. 12). The vacuum level V_0 lies 2.35 eV above the ground state of Na^-. The optical spectrum contains transitions to a tightly bound Na^-* as well as to a conducting state of quasi-free electrons. The bottom of the conduction band, as determined by measuring the band gap from the temperature dependence of the conductivity, lies ~ 0.15 eV below V_0. The fluorescence then originates from the bottom of the conduction band into the ground state as a sort of electron-hole recombination. Trapped electron states exist at ~ 1.7 eV below V_0.

The low-energy "tail" in the PEE spectra indicates that shallower electron traps are also present at lower concentrations.

The other sodides are expected to have similar energy schemes. The softer structure results in a wide distribution of e_t^- states. We expect that they also will show photoluminescence which could then be used to probe the excited state.

The origin of the striking temperature dependence of the quantum yield from both Na^- and e_t^- is not clear. It seems to be connected with the resistivity of the films but does not show the saturation characteristics expected for a space-charge-limited photocurrent within the solid. The only other explanation which we have for this temperature dependence is a variation of the joint density of states with temperature originating from the thermal expansion of these rather "soft" materials.

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