

Intrinsic Optical Properties of Alkali Halides

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Dielectric constants for KI, KBr, and KCl are deduced from reflectance data between 1 and 25 eV. The data may be described unambiguously in terms of individual particle and collective excitations. Strong absorption peaks originating from both the anion and the deeper lying $K^+ 3p$ band are believed to be associated primarily with excitons. The presence of collective effects is indicated by a plasma resonance which corresponds roughly to an electron density of six per molecule. It occurs in a spectral region where damping effects due to individual particle excitations from both filled bands are weak. A qualitative argument, based on a treatment of the many electron problem in the Hartree-Fock approximation, is given to show why excitons should predominate over ordinary interband transitions in alkali halides. Photoelectric emission data are re-examined and shown to be compatible with this viewpoint.

1. INTRODUCTION AND EXPERIMENTAL RESULTS

THE absorption spectrum of the alkali halides consists of a series of peaks which persist to the regions of the far vacuum ultraviolet.¹ Such data have been available in the literature for some time; but detailed interpretation has been given only to structure occurring at lowest energy.^{2,3} In fact, it has been just recently that experiments on photoelectric emission,⁴ photoconductivity,⁵ and luminescence⁶ have given values for the band gaps in these crystals.

The approach of the present paper is to apply the techniques which have proven successful in the interpretation of the optical properties of semiconductors⁷

and metals⁸ to the alkali halides. Experimentally, the normal incidence reflectance spectrum of single crystal specimens, like that shown in Fig. 1 for KCl, KBr, and KI, is measured. The Kramers-Kronig relations are applied to these data to obtain the dielectric constants which describe the optical properties. The behavior of the dielectric constants in any region of the spectrum can then be analyzed according to the theories which apply to the various possible optical excitations of the crystal. In the case of the semiconductors and metals previously investigated, the interpretation was greatly aided by results of detailed band-structure calculations. For the alkali halides, this guide is not available to nearly the same extent. Howland's⁹ calculations consider only the valence bands. Bassani's¹⁰ estimates, based on a perturbation of the empty lattice and point-ion approximation are more complete although somewhat preliminary at the present time.

More important, perhaps, is the question as to whether the results of band theory are applicable at all to the alkali halides. The dielectric constants for these crystals are small compared to those typical of semiconductors like silicon and germanium and thus the Coulomb interaction is correspondingly more effective. If the calculations of the excited electron states of the crystal are based on a theory which neglects the Coulomb interaction between the electron and hole (exciton states), then interpretation based on this simple band picture may be impossible when this interaction is strong.

Since the early measurements of Hilsch and Pohl,¹¹ exciton states have been regarded as important in the optical-absorption spectrum of the alkali halides at low energy.^{2,3} One of the principal points to be made in this paper is that exciton states are likely to be present as well at higher energies where they are degenerate with continuum states. Such continuum states also play a role in the optical properties of alkali halides.

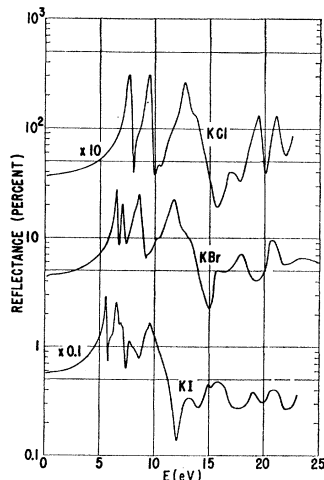


FIG. 1. Spectral dependence of the reflectance of the KCl, KBr, and KI.

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¹ J. E. Eby, K. J. Teegarden, and D. B. Dutton, *Phys. Rev.* **116**, 1099 (1959); A. Smith, *ibid.* **44**, 520 (1933).

² F. Fischer and R. Hilsch, *Nachr. Akad. Wiss. Gottingen II. Math. Physik, Kl.* **1959**, No. 8 (1959).

³ H. Haken, *Fortschr. Physik* **6**, 271 (1958). R. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York) (to be published).

⁴ H. R. Philipp and E. A. Taft, *J. Phys. Chem. Solids* **1**, 159 (1956); E. A. Taft and H. R. Philipp, *ibid.* **3**, 1 (1957).

⁵ K. J. Teegarden, U. S. Air Force Technical Note AFOSR TN-59-303, 1959 (unpublished).

⁶ T. Timusk and W. Martienssen, *Phys. Rev.* **128**, 1656 (1962).

⁷ H. R. Philipp and H. Ehrenreich, *Phys. Rev.* **129**, 1550 (1963).

⁸ H. Ehrenreich and H. R. Philipp, *Phys. Rev.* **128**, 1622 (1962).

⁹ L. P. Howland, *Phys. Rev.* **109**, 1927 (1958).

¹⁰ We are indebted to F. Bassani for communicating these results to us.

¹¹ R. Hilsch, and R. W. Pohl, *Z. Physik* **57**, 145 (1939); **59**, 812 (1930).

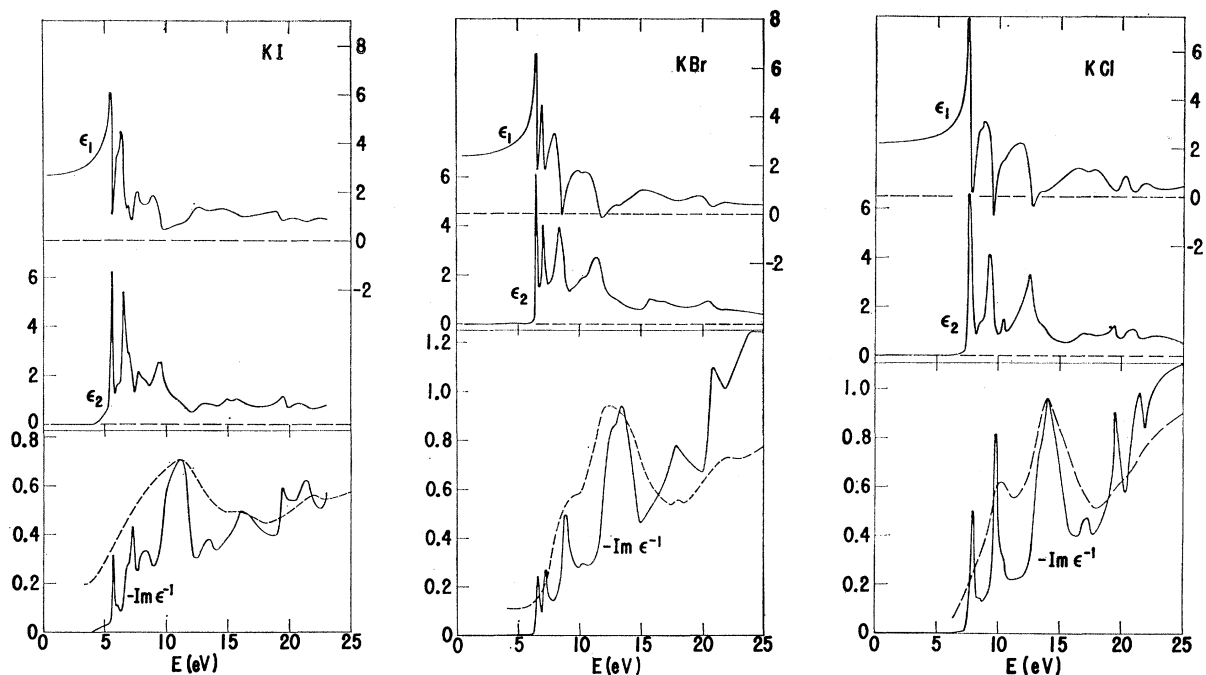


FIG. 2. Spectral dependence of the real and imaginary parts of the dielectric constant, ϵ_1 and ϵ_2 , and the energy loss function $-\text{Im}(\epsilon^{-1})$ for KCl, KBr, and KI. The results of characteristic energy loss experiments by P. E. Best (Ref. 16) are shown by the dashed curve.

We shall define them in terms of their ability to maintain photoconductivity. Because of the strength of the Coulomb interaction, and the tightly bound character of electrons in the valence band, transitions to these states will be seen to be much weaker than those associated with many of the exciton states.

Plasma oscillations, which are also associated with the Coulomb interaction, will be shown to be present in the alkali halides. They are damped relatively weakly since they occur energetically in that region of the spectrum where the oscillator strength for the upper filled band is essentially exhausted and where transitions from the next deeper band are weak. This situation is analogous to that observed in the semiconductors previously studied.⁷

Values for the real and imaginary parts of the dielectric constants, ϵ_1 and ϵ_2 , and the energy-loss function $\text{Im}\epsilon^{-1}(\omega)$, deduced from the data in Fig. 1, are presented in Sec. 2. In addition, we discuss, in this section, conclusions which follow directly from the experimental results. Section 3 presents a qualitative theoretical discussion of the role of excitons and plasmons in alkali halides which is intended to justify the preceding statements. In Sec. 4, the results of photoelectric-emission studies are interpreted in the framework of the present paper.

2. EXPERIMENTAL CONCLUSIONS

As shown in Fig. 2, the dielectric constants corresponding to the lowest energy-absorption peak (cf.

Fig. 3) are oscillator-like. This peak has indeed long been recognized as an exciton state. A second oscillator-like peak in the absorption spectrum occurs at an energy which is higher than the first by approximately the spin-orbit splitting of the halogen atom ground state. This splitting is about 0.1 eV for the chlorides, 0.4 eV for the bromides, and 0.9 eV for the alkali iodides. In KCl, this doublet is not clearly resolved at room temperature while, for KI, it occurs in a region where additional structure is present.

The onset of interband transitions in the alkali halides (iodides) has been related to a weak, "edge-like" absorption step which occurs on the high-energy side of the first exciton peak.⁴ Thus, for the alkali iodides at least, the second strong exciton peak is degenerate

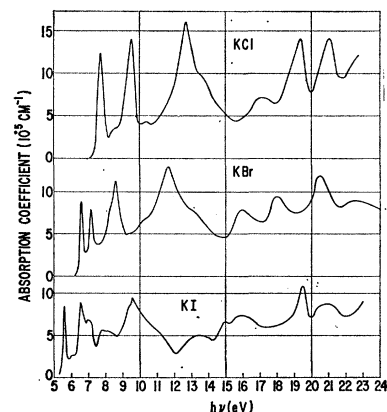


FIG. 3. Spectral dependence of the absorption coefficient ($\alpha = 4\pi k/\lambda$) for KCl, KBr, and KI.

with transitions to band states which result in free electrons and holes. Figure 2 shows that the strong structure at higher energies is also oscillator-like. This behavior contrasts with that generally observed in semiconductor materials where interband transitions at critical points, rather than excitons, predominate.

The strength of optical absorption in the first exciton peak compared to that associated with interband transitions decreases as one passes to the halides of the lighter alkali metals.^{1,4} This is the direction of increasing dielectric constant and decreasing lattice constant. For the silver halides, having still higher dielectric constant, the first exciton peak is practically immersed in the continuum at room temperature.¹²

Plots of the energy-loss function $-\text{Im}\epsilon^{-1} = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2)$ are also shown in Fig. 2. This function exhibits small peaks in the vicinity of the oscillator-like absorption bands described above. A broader, stronger maximum, which occurs in the energy range 11 to 14 eV for the three crystals described in Fig. 2, does not correspond directly to structure in optical absorption. Instead it is associated with a somewhat broadened plasma resonance since ϵ_1 and ϵ_2 are small in the vicinity of the peak and have positive and negative slope, respectively. Here $\epsilon(\omega_P) = 0$, where $\omega_P = \omega_{Pr} - i\omega_{Pi}$ is a complex frequency whose real part is the plasma frequency and whose imaginary part describes the extent to which the plasma oscillations are damped. For a free-electron gas at 0°K and for long wavelengths, $\epsilon_1(\omega_P) = \epsilon_2(\omega_P) = 0$. For real crystals this condition is highly approximate and may, in fact, not be realized. In Fig. 2 we observe that while ϵ_1 is small in this region for all the crystals it remains positive in the case of KI.¹³ Because the structure in the dielectric constants associated with individual particle excitations is quite different from that corresponding to plasma oscillations, it is possible to distinguish unambiguously between these by the present experimental results. Since the

oscillator strength for individual particle excitations is relatively weak in the region of the plasma resonance, the observed values of 11.4, 13.5, and 14.0 eV for KI, KBr, and KCl, respectively, are not changed substantially from the computed values of 9.7, 10.7, and 11.5 eV corresponding to six free electrons per molecule.¹⁵

The curve calculated from the dielectric constants is compared with the characteristic energy loss data of Best¹⁶ in Fig. 2. The electron scattering data are clearly not as detailed as the results obtained from optical data, although the main features are well represented by them.

In discussing the optical properties of semiconductors⁷ and metals,⁸ use was made of two integrals involving the imaginary part of the dielectric constant. The first of these,

$$\int_0^{\omega_0} \omega \epsilon_2(\omega) d\omega = (2\pi^2 N e^2 / m) n_{\text{eff}}, \quad (1)$$

evaluates n_{eff} , the effective number of free electrons contributing to the optical properties in the range to ω_0 . These curves, shown in Fig. 4 for KI, KBr, and KCl, present strong evidence that deeper lying bands contribute to the optical properties of these crystals for photon energies greater than about 15 eV. According to Howland's calculations, the valence band of KCl is the $\text{Cl}^- 3p$ and the next lower one is the $\text{K}^+ 3p$ band. The wave functions for these two bands are well isolated with little overlap, and, consequently, there is little oscillator strength coupling of the type that connects the valence and d bands of semiconductors.⁷ The curve for n_{eff} would, therefore, be expected to saturate at six electrons per molecule. The curves in Fig. 4 do not, in fact, show marked saturation at $n_{\text{eff}} = 6$ electrons/molecule but rise steadily above this value, presumably because of excitations from the deeper lying cation

¹² Y. Okamoto, Nachr. Akad. Wiss. Göttingen, Math. Physik Kl. IIa 1956 No. 14 (1956); S. Tutihasi, Phys. Rev. **105**, 882 (1957).

¹³ The region of plasma oscillations is denoted by characteristic structure in the reflectance spectrum: mainly a sharp decrease in the curve for R as is seen in Fig. 1. This behavior is determined by the form of the dielectric constants for collective oscillations and should thus be relatively independent of the particular material under discussion. The reflectance R and phase angle θ are given by $R = [(n-1)^2 + k^2] / [(n+1)^2 + k^2]$, and $\tan\theta = -2k / (n^2 + k^2 - 1)$, where n and k are the optical constants. The conditions for plasma oscillations imply $n \cong k \ll 1$ (ϵ_1 and ϵ_2 small) and in the vicinity of the plasma frequency the above equations reduce to $R \cong (1-2k)/(1+2k) \cong 100\%$ and $\tan\theta \cong 2k$ ($\theta \cong -180^\circ$, an angle in the third quadrant). The latter equation, together with the Kramers-Kronig relation [Eq. (2) of Ref. 14], implies that $dR/d\omega$ must be large and negative in the vicinity of the plasma frequency while the approximation for R implies that the decrease in reflectance takes place on the high-energy side of the plasma frequency. This effect broadens increasingly as damping becomes more important. The fact that plasma oscillations in real crystals are often characterized by a dip in the reflectance, rather than a simple decrease, is due to the onset of further individual particle excitations at higher energies. This is well illustrated by the sharp reflectance minimum near 4 eV in Ag (see Ref. 8).

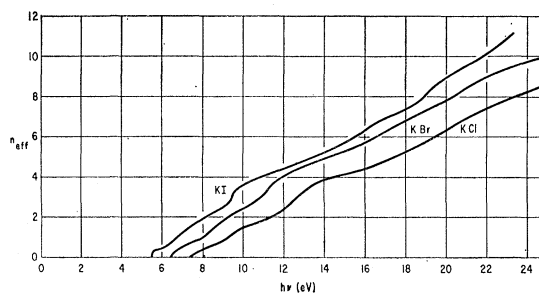


FIG. 4. Effective number of electrons per molecule versus E obtained from numerical integration of experimental ϵ_2 using Eq. (1).

¹⁴ H. R. Philipp, and E. A. Taft, Phys. Rev. **113**, 1002 (1959).

¹⁵ Best (Ref. 16) compares the results of characteristic energy loss experiments with computed values of the plasma frequency corresponding to eight free electrons per molecule. According to Howland (Ref. 9) the valence band of KCl is the $\text{Cl}^- 3p$ band of density six electrons per molecule. The $\text{Cl}^- 3p$ band, in fact, lies deeper than the $\text{K}^+ 3p$ band.

¹⁶ P. E. Best, Proc. Phys. Soc. (London) **79**, 133 (1962).

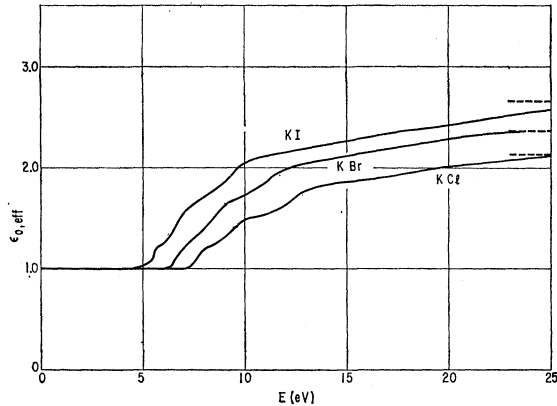


FIG. 5. $\epsilon_{0,\text{eff}}$ versus E for KCl, KBr, and KI. The dielectric constants obtained from Ref. 17 are indicated by dashed-line segments.

p bands. The fact that the n_{eff} is near six in the region of plasma resonance indicates that the oscillator strength for valence band excitation is essentially exhausted. This situation applies to each of the crystals discussed here.

The second integral,

$$\epsilon_{0,\text{eff}} = 1 + \frac{2}{\pi} \int_0^{\omega_0} \omega^{-1} \epsilon_2(\omega) d\omega, \quad (2)$$

defines $\epsilon_{0,\text{eff}}$, the effective dielectric constant associated with optical transitions in the energy range to ω_0 . The curve for $\epsilon_{0,\text{eff}}$ should saturate at a value near that corresponding to the independently measured dielectric constant¹⁷ above the reststrahlen frequency as is seen in Fig. 5. In contrast to semiconductors, where the principal band gaps contributing significantly to ϵ_0 lie below about 5 eV, the band gaps contributing appreciably to ϵ_0 in the alkali halides are dispersed over a much wider energy range.

This integral may be considered to be an experimental self-consistency test of the Kramers-Kronig relations connecting ϵ_1 and ϵ_2 . By contrast, the contribution to n_{eff} from core states is so significant that these plots cannot be used to establish any possible contradiction to the present form of the Kramers-Kronig relations resulting from spatial dispersion effects.¹⁸

3. ROLE OF EXCITONS AND PLASMONS

The description of the excited electronic states of a crystal by band theory neglects the change in the Coulomb energy, within the Hartree-Fock approximation, introduced when an electron is transferred from a valence to a conduction band. When the Coulomb terms are properly modified, the excited energy levels of the crystal are altered. The description now includes excitons as intrinsic excitations of the system.

¹⁷ *Synthetic Optical Crystals* (Harshaw Chemical Company, Cleveland, 1955).

¹⁸ A. A. Rukhadze and V. P. Silin, *Usp. Fiz. Nauk* **74**, 223 (1961) [translation: *Soviet Phys.—Usp.* **4**, 459 (1961)].

The reduction of the general Hamiltonian of the system which yields these results is *almost* identical with that producing plasma oscillations in the random-phase approximation (RPA). The density matrix formalism used in this connection¹⁹ is particularly convenient since the density matrix $\rho(x, x')$ in the coordinate representation is just the exciton wave function. As previously pointed out, two essential approximations are necessary to reduce the Liouville equation for the general system to that appropriate in the RPA: (1) linearization (the Coulomb interaction is regarded as weak), and (2) factorization (the average of the product of density matrices appearing in the Coulomb term is separated into the product of the separate averages). Excitons are possible eigenstates of the system if the factorization is made antisymmetrically, so that in addition to the direct Coulomb terms characteristic of the Hartree approximation, one also obtains exchange terms. The predominance of the latter, together with their negative sign, causes the Coulomb interaction between electron and hole to be attractive and to produce a bound state. On the other hand, it is the direct Coulomb terms which are responsible both for the migration of excitons through crystals, and for plasma oscillations as normal modes. Indeed, it was only these terms which were considered in the treatment of Ref. 19.

In accordance with the prescription supplied by Hubbard²⁰ and Anderson,²¹ the exchange interaction should be screened by the dielectric constant. This provision yields the proper Coulomb interaction, appropriate to the crystal, between the electron and hole.

The formalism, just outlined, is very simple and useful since its relationship to other treatments of the many-body problem, particularly of Sawada *et al.*, and Brout,²² has already been established. In the present paper we shall confine ourselves to a qualitative description of the results pertinent to the experiments described here. One of us hopes to present in the near future a more explicit and formal discussion of these matters.

In order to understand the effect of excitons (in contrast to ordinary interband transitions) on the optical properties, it is helpful to consider a fairly localized region of k space surrounding a minimum band gap separating a filled and empty band where an exciton may be formed from a linear combination of the band functions in this region. This region may be energetically degenerate with other regions in k space where the excited states form a continuum. Because we are dealing here with optically excited states in a region of high-absorption coefficient, it is sufficient, in the absence of Coulomb interactions, to consider

¹⁹ H. Ehrenreich and M. H. Cohen, *Phys. Rev.* **115**, 786 (1959).

²⁰ J. Hubbard, *Proc. Roy. Soc. (London)* **A240**, 539 (1957).

²¹ P. W. Anderson, *Phys. Rev.* **112**, 1900 (1958).

²² K. Sawada, K. A. Brueckner, W. Fukuda, and R. Brout, *Phys. Rev.* **108**, 507 (1957); R. Brout, *ibid.* **108**, 515 (1957).

only vertical excitations. We suppose there to be N such states in this region (equal to the number of states in either the valence or conduction band). As the Coulomb interaction is turned on, N new states α are formed, some of which may be excitons. For simplicity, it will be assumed that the mixing of basic states k is confined to the two bands in question, and to this restricted region of k space, although in principle, of course, any number of bands could be involved. This approximation represents a restriction on the permissible strength of the Coulomb considered more tightly bound than the hydrogenic type. The region of k space involved is also limited by this approximation. Its radius must be smaller than the distance to a critical point in the joint density of states separating two minimum gaps, or the distance to a branch point in complex k space corresponding to the intersection of the two bands in question.²³

This assumption also seems reasonable from an experimental view since the binding energies of the previously identified excitons in the alkali halides are rather smaller than the band gap. Fischer and Hilsch,² in fact, interpreted them as members of a purely hydrogenic series. While this view probably represents an oversimplification of the actual situation, we do think it likely that these excitons are describable in terms of Coulomb interactions having a strength of the sort envisioned here.

By explicit consideration of the transformation from the purely interband states k to the new states α , which include the excitons, one can show that the *total* oscillator strength corresponding to this particular region in k space and the two bands is approximately conserved as the Coulomb interaction is turned on. Since the valence band functions in the alkali halides are reasonably well localized, a deeper exciton state will absorb more oscillator strength from this region than a shallow exciton state. Stronger binding implies a smaller exciton radius, larger overlap between electron and hole wave functions, and a correspondingly greater momentum matrix element. This type of argument is exemplified by Elliott's proof²⁴ that for a hydrogenic exciton the oscillator strength of the first line is of order (atomic radius/exciton radius).³ Thus, an exciton whose binding energy is somewhat greater than hydrogenic may absorb most of the oscillator strength of the entire region.

The predominance of exciton over interband effects in the alkali halides may be associated with their relatively small dielectric constants and large lattice parameters. In the alkali halides $\epsilon_1(0) \sim 2-3$, whereas in

silver halides $\epsilon_1(0) \sim 4-5$ and in typical semiconductors $\epsilon_1(0) \sim 10-16$.²⁵ The Coulomb interaction is, therefore, correspondingly stronger in the materials under consideration here. In particular, according to the hydrogenic model, the exciton Bohr orbits in the alkali halides will be some five times smaller than in semiconductors. This, together with the fact that the interatomic distance is twice as big as in semiconductors, implies that the smallest orbit extends only to nearest neighbors. Since the existence of hydrogenic excitons requires that the binding energy relative to the band gap be small so that the effective mass approximation is valid, and, in addition, a separation of electron and hole which is rather larger than the extent of their wave functions, the lowest exciton states in the present alkali halides will probably not be hydrogenic.

The preceding arguments are valid in many cases for excitons involving conduction bands lying energetically higher than the lowest edge. It should be remembered, however, that the state so formed will now be degenerate with continuum-like states in other regions of k space and might be expected to decay rapidly. Furthermore, excited conduction bands become increasingly broader: The effective masses are, therefore, likely to be smaller and the exciton radii larger. As a result, the oscillator strengths may be correspondingly reduced. The experimental facts, however, indicate that the structure at energies greater than the lowest exciton peaks continues to be predominantly oscillator-like and characteristic of excitons. It is true that there is an oscillator-like peak in each of the Group IV and III-V semiconductors studied so far,⁷ which in the case of²⁶ Si and²⁷ Ge has been shown to

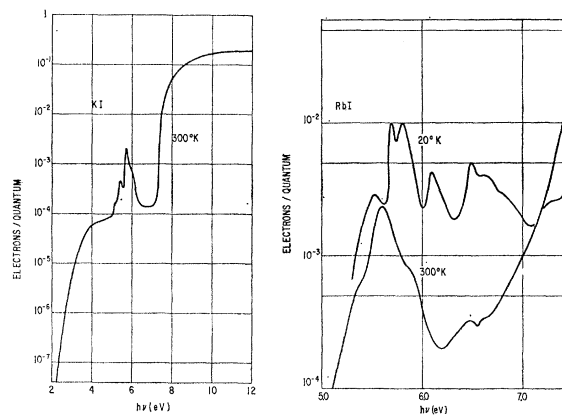


FIG. 6. (a) Spectral distribution of the photoelectric yield at 300°K for KI sample containing F centers [after Taft and Philipp (Ref. 4)]. (b) Detailed measurements in the energy range 5 to 7 eV of the photoelectric yield at 300 and 20°K for a RbI sample containing F centers.

²³ The latter restriction arises because the function $\epsilon_l(\partial\nabla) - \epsilon_l'(\partial\nabla)$, where ϵ_l is the Hartree-Fock energy corresponding to band l , is interpreted as a Taylor expansion about the minimum gap. The validity of such an expansion is limited by the location of branch points. It should be noted also that while the condition for the equality of electron and hole velocities, $\epsilon_l(\partial\nabla) = \epsilon_l'(\partial\nabla)$ is satisfied for any critical point in the joint density of states, we assume here that only regions surrounding minima can give rise to bound electron-hole states.

²⁴ R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

²⁵ The dielectric constant appropriate for all but rather shallow exciton states is that valid for frequencies *greater* than the reststrahlen frequency. This point has been discussed very thoroughly by Haken (Ref. 3).

²⁶ D. Brust, M. H. Cohen, and J. C. Phillips, Phys. Rev. Letters **9**, 389 (1962).

²⁷ D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters **9**, 94 (1962).

result from the confluence of two saddle points. Such a situation could conceivably occur as well in the alkali halides; however, it is difficult to understand how this could be the case for almost every observed peak.

The exciton lifetime problems just mentioned are very similar to those corresponding to excitations at critical points in semiconductors whose excitation energy is degenerate with a continuum characterized by a slowly varying density of states. The well-established fact that in semiconductors it is possible to observe sharp structure in the optical constants under these circumstances leads to the plausible analogy that in the alkali halides the same might be true for the corresponding excitons, since these are also associated with critical points. The theoretical treatment of these questions from first principles is very difficult since the damping of these states is probably associated with the electron-electron interaction or possibly tunneling processes. Since normal electron-electron scattering processes in parabolic free-electron-like bands do not destroy the current induced by the light wave, the significant interactions are probably of the umklapp variety (involving a reflection from a Bragg plane) or associated with regions of the Brillouin zone which are not free-electron-like.

Excitons may be associated also with excitations from deeper valence bands. The interpretation given to some features of the x-ray spectra in alkali halides by Parratt and Jossem²⁸ as well as Friedel²⁹ invokes just such states.

The formalism qualitatively described at the beginning of this section also includes plasmons as possible excitations of the system. As already pointed out, the experimentally observed plasma excitations lie in an energy range where the oscillator strength corresponding to both the Cl^- (or Br^- , I^-) p and the K^+ $3p$ bands are weak. Since the total oscillator strength associated with each pair of bands is constant for the case of moderately strong Coulomb interactions independent of whether excitons are being considered or not, the asymptotic form of the dielectric constant in the region where the oscillator strength corresponding to the valence band has been exhausted will be the same as in the RPA: $\epsilon(\omega) \approx 1 - \omega_p^2/\omega^2$, where $\omega_p^2 = 4\pi n e^2/m$, n is the density of valence electrons, and m is the free-electron mass. This explains why the observed plasma frequency is reasonably close to that expected for free electrons having a density of six per molecule. However, in the present case, the oscillator strengths are not completely vanishing and strong individual particle excitations occur in the vicinity of the peak of the energy-loss function. Thus, $\epsilon(\omega)$ will contain additional relatively small complex terms which shift the plasma frequency and damp the excitation.

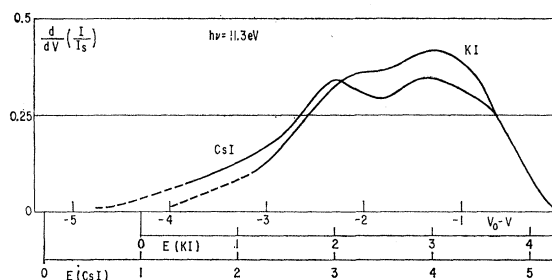


FIG. 7. Energy distribution of intrinsic photoelectrons from KI and CsI for $h\nu = 11.3$ eV. The uppermost abscissa scale gives $V_0 - V$ in volts, where V_0 is the "stopping potential" corresponding to the Einstein maximum photoelectron energy, where \bar{V} is the retarding potential. The lower abscissa scales give the kinetic energy E of photoelectrons from KI and CsI, respectively, in eV. The ordinate gives directly the derivative of the current voltage characteristic for the spherical-condenser phototube; I is the photocurrent at applied potential V ; I_s is the saturation current [after Philipp, Taft, and Apker (Ref. 31)].

4. DISCUSSION OF PHOTOELECTRIC EMISSION

Photoelectric-emission results may be interpreted in a fashion consistent with the viewpoint taken in this paper. We shall use measurements on several alkali iodides as the basis for the following discussion. The photoelectric yield at 300°K for⁴ KI is shown in Fig. 6(a). More detailed curves of the extrinsic yield below 7 eV are shown in Fig. 6(b) for an RbI sample at 300 and 20°K.³⁰ Measurements of the energy distribution of emitted photoelectrons from KI and CsI are shown in Fig. 7 for an incident quantum energy of 11.3 eV.³¹ The following features are noted in these curves and will be discussed in turn in the paragraphs below: (1) When the incident photon energy is increased beyond 7 eV, the yield rises rapidly and reaches efficiencies greater than 10%. In this region there is no structure corresponding to peaks in the optical absorption spectrum. (2) When F centers are present an extrinsic yield is observed below 7 eV. Peaks in this region, which coincide with absorption structure, are associated with exciton-induced emission from F centers.³² The yield is considerably greater for peaks which occur energetically below the band gap than for those which lie above the shoulder attributed to the onset of interband transitions. (3) Energy distribution curves of intrinsic photoelectrons show broad structure. For CsI, the shape of the distribution is independent of photon energy in the range 10.3 to 11.3 eV except for a shift on the kinetic energy axis. At 11.3 eV there is a distinct sparsity of slow electrons. For the alkali iodides, the widths of the energy distributions at maximum photon energy are 3–4 eV.

1. The lack of structure in the intrinsic photoemission is in marked contrast with the behavior of the optical properties over the same energy range. In crystals,

³⁰ E. A. Taft, H. R. Philipp, Bull. Am. Phys. Soc. **5**, 201 (1960).
³¹ H. R. Philipp, E. A. Taft, and L. Apker, Phys. Rev. **120**, 49 (1960).

³² L. Apker, and E. A. Taft, Phys. Rev. **79**, 964 (1950); **81**, 698 (1951); **82**, 814 (1951).

²⁸ L. G. Parratt, Rev. Mod. Phys. **31**, 616 (1959).

²⁹ J. Friedel, Phil. Mag. **43**, 153 (1952).

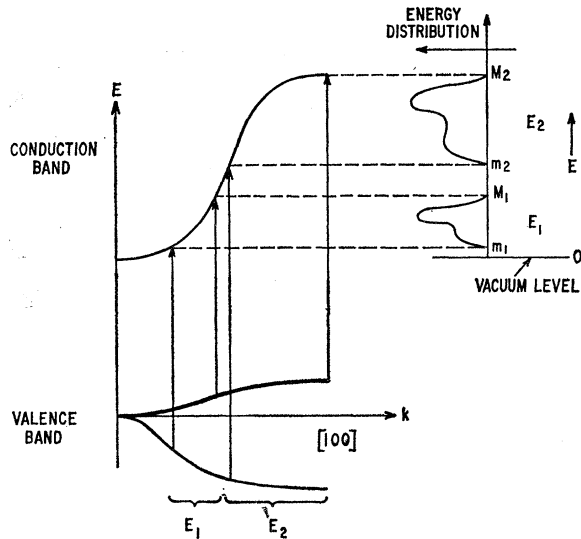


FIG. 8. Simple two-band model relevant to the interpretation of energy-distribution measurements.

such as KI or cesiated Si having a small electron affinity, the photoelectron emission may or may not show structure depending on the number of strong optical transitions terminating above the vacuum level. Structure associated with interband transitions has been observed in cesiated Si and has been interpreted in terms of final states above and below the vacuum level.³³ The absence of comparable structure in the alkali halides shows that practically all excited electrons are able to leave the crystal. Thus, energy loss and adverse band-bending effects must be small to account for the high yield of these crystals. The smoothness of the yield curve also implies that the escape depth for excited photoelectrons is considerably larger than the absorption length for the photons. In addition, excitons corresponding to higher bands (above the vacuum level) must dissociate into free electron-hole pairs such that the electron lies above the vacuum level. This dissociation is always possible via the Coulomb interaction since such excitons are energetically degenerate with continuum states.

2. It is possible for an exciton of energy greater than the band gap to decay either via the excitation of an F center or by dissociation into an electron-hole pair. The less efficient induced emission from F centers due to excitons whose energy is greater than the band gap may indicate that the latter mechanism is dominant. The interaction with the F center in this case is likely to involve only one of the two dissociated particles with no resulting electrons above the vacuum level.

3. In previous studies of the energy distribution of photoelectrons, the observed structure has been associated with the variation of the density of states of the valence band. The relative insensitivity of this structure

to photon energy has been attributed to an approximately energy-independent density of states in the conduction band. In point of fact, however, the strong structure in the optical properties of solids is associated with critical points in the *joint* density of states^{26,34} involving the two bands in question and not each band alone. This fact was not considered in previous experimental interpretations. However, in the absence of band calculations, it is still not possible to account in any specific way for the broad structure observed in these distributions and its dependence on $h\nu$. Transitions involving both interband and exciton states may contribute differently and in a complicated way to structure in these curves.

To illustrate the possible modifications introduced by the present viewpoint, let us consider the simple two-band model presented in Fig. 8. We consider a valence band having p symmetry and a conduction band having s symmetry as shown schematically for the [100] direction in a face-centered cubic lattice. The photons will induce vertical excitations between continuum states of the type indicated in the diagram. For a given energy of excitation E , the emitted photoelectrons will have a minimum and maximum energy m and M relative to the vacuum level. If the excitations shown are stronger in comparison to others in the Brillouin zone having intermediate energy, the energy distributions shown in the figure may result. The structure given these distributions is associated with the double degeneracy of the upper valence band, drawn as a heavier line in Fig. 8, along [100] directions.

The main points to be made in connection with this model are: (1) The energy differences $M-m$ corresponding to E_1 or E_2 are not necessarily characteristic of the width of the valence band. This band is, in fact, broader than indicated by these differences. (2) The absence of slow electrons in the energy distributions does not necessarily imply that one has excited electrons from the bottom edge of the valence band.

We have not considered exciton states nor critical points in the joint density of states in the present model. Clearly, strong absorption effects associated with either mechanism can appreciably alter the energy distribution. To illustrate this fact we have purposely drawn the arrow corresponding to M of E_2 in Fig. 8 at a critical point to emphasize the fact that when the optical properties associated with such a point are rapidly varying, as they are at low energy, the structure associated with this point can be quite different from that associated with M of E_1 .

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