Photoemission and Valence Band Structure of Alkali Iodides*

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(Received May 16, 1960)

Energy distributions are described for external photoelectrons ejected from CsI by photons of energy 11.3 ev. All but about 5% of the photoelectrons emerge with kinetic energies between 1.5 ev and 5.3 ev. The conspicuous lack of electrons at lower energies is interpreted in terms of a valence band of width about 3 or 4 ev with an upper edge lying about 6 ev below the vacuum level. Related results are mentioned for RbI, KI, NaI, CsBr, and CsCl.

INTRODUCTION

INTRINSIC photoemission from alkali halides occurs with high yield, usually in excess of 0.1 external photoelectron per incident photon. From a study of this conveniently efficient process, the position of the top of the valence band relative to the vacuum level has been estimated in two ways.[1] First, the threshold photon energy (on a graph of the spectral distribution of intrinsic photoemission) furnishes a direct measure of the valence band position. Second, the energy distribution of the intrinsic photoelectrons shows a relatively sharp upper limit that can be related to the position of the valence band edge by straightforward application of Einstein's photoelectric equation. In the absence of a quantitative theory of the forms of the spectral and energy distributions, one cannot at present do this rigorously.[2] Nevertheless, semiquantitative estimates appear to be meaningful within a few tenths of an electron volt. This is precise enough to be very useful. Information thus obtained has been valuable for comparison with the results of other investigations dealing, for example, with the onset of interband transitions in optical absorption spectra,[1,3] with the threshold photon energy for intrinsic photoconductivity,[4] and with the relation between excitation processes and interband transitions.[5]

By photoelectric methods, it is possible to get still further information about the electronic energy structure in alkali halides. This is the subject of the present paper. We discuss the kinetic energy spectra of intrinsic photoelectrons that are ejected from CsI and RbI by photons of energy up to 11.3 ev. These spectra have two interesting and unusual characteristics. Most of the photoelectrons emerge in a band of kinetic energies about 3 or 4 ev wide, electrons of low energy being conspicuously absent. Further, there is reproducible structure within the energy distribution. These findings we interpret as evidence that the valence bands in these iodides are 3 or 4 ev wide, and that there is experimentally resolvable structure within them.

EXPERIMENTAL DETAIL

Energy distributions were determined by retarding-potential methods. The phototubes had spherical collectors and "bucket type" interchangeable emitters like those used in previous work.[6] However, they were made smaller in order to fit into the space available in the vacuum monochromator.[7] Collector diameters were about 8 cm, and the buckets were about 4 mm on an edge. Lithium fluoride windows, which were cemented on, admitted incident photons with energies up to 11.3 ev. The use of cement for sealed-off phototubes may lead to questionable vacuum conditions, of course. For these ionic crystals, however, we do not think the results are seriously affected.[1]

In making energy distribution measurements by retarding potential techniques, a very important point arises when crystals like the alkali halides are concerned. This involves the electric field outside the emitter surface. The solid is usually not in a state of thermal and electrical equilibrium, since metastable defects such as color centers are produced during irradiation with energetic photons. Thus, there is neither an equilibrium Fermi level in the sample nor an equilibrium contact potential outside it. An effective contact potential may be determined from the measurements, however. No serious difficulty arises if it is recognized that this quantity may change in a nonequilibrium fashion, and if the relation between retarding field and applied voltage is determined accordingly.[8]

* Presented in part at the meeting of the American Physical Society, Cleveland, Ohio, November 28, 1959. See Bull. Am. Phys. Soc. 4, 427 (1959).
[1] H. R. Philipp and E. A. Taft, J. Phys. Chem. Solids 1, 159 (1956); E. A. Taft and H. R. Philipp, J. Phys. Chem. Solids 3, 1 (1957).
[2] See, for example, remarks bearing on this question by I. M. Dykman and K. B. Tolpygo in a discussion of the paper by P. G. Borzyak, V. F. Bibik, and O. G. Sarbei, Izvest. Akad. Nauk (U.S.S.R.) 22, 574 (1958) [translation: Bull. Acad. Sci. S.S.R. 22, 565 (1958)]. In the present paper, although we determine the values of the intrinsic photoelectric thresholds and the widths of the valence bands only in a semiquantitative and somewhat naive way, we consider that the intrinsic emission is clearly separable from extrinsic and that the important concepts are clear.
[3] W. Martienssen, J. Phys. Chem. Solids 2, 257 (1957); J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. 116, 1099 (1959); P. L. Hartman, J. G. Siegfried, and J. R. Nelson, Phys. Rev. 105, 23 (1957).
[4] K. J. Teegarden, Air Force Office of Scientific Research Report 59303, April 10, 1959 (unpublished); D. L. Dexter, J. Phys. Chem. Solids 8, 473 (1959); L. Apker, J. Phys. Chem. Solids 8, 538 (1959); J. W. Taylor and P. L. Hartman, Phys. Rev. 113, 1421 (1959).
[5] F. Fischer and R. Hilsch, Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. No. 8, 241 (1959); E. A. Taft and H. R. Philipp, Bull. Am. Phys. Soc. 5, 201 (1960).

[6] L. Apker and E. Taft, Phys. Rev. 79, 964 (1950); 82, 814 (1951).
[7] P. D. Johnson, J. Opt. Soc. Am. 42, 278 (1952).
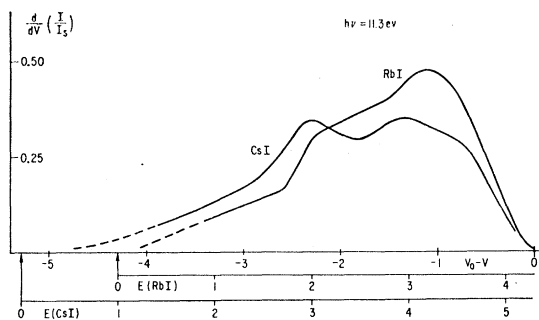[8] In the second paper of footnote 6, see part III. The effective

FIG. 1. Energy distribution of intrinsic photoelectrons from RbI 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 (located by approximate extrapolation techniques), and where V is the retarding potential in the usual type of spherical phototube.[1] The lower abscissa scales give the kinetic energy E of photoelectrons from RbI and CsI, respectively, in electron volts. 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. The broken lines show portions of the curves which do not shift linearly with $h\nu$. Errors in ordinates are about ± 0.05 or less.

RESULTS AND DISCUSSION

Figure 1 shows energy distributions of the intrinsic photoelectrons ejected from RbI and CsI by photons of energy 11.3 ev. The spectral distributions of the photoelectric yields for these samples were like those given before.[1] Thus, the intrinsic photoelectric threshold energies were about 6 ev for CsI and about 7 ev for RbI. Accordingly, in Fig. 1, intrinsic photoelectrons should appear with kinetic energies ranging from 0 to 5.3 ev for CsI and from 0 to 4.3 ev for RbI. The data follow the expected behavior at the higher kinetic energies but depart from it drastically at low energies. Specifically, there is a pronounced sparsity of electrons with energies in the range from 0 to 1.5 ev for CsI. All but 5% lie above this range. The same effect is evident for RbI, although it is not so striking, since the intrinsic photoelectric threshold is about 1 ev higher; in this case, all but 3% of the electrons emerge with energies in excess of 0.8 ev.

This type of behavior is quite unusual. In practically all previously known cases in fact, photoelectrons are concentrated (rather than lacking) at these lower energies, because complicated excitation processes or electron

contact potential may also be nonuniform over the surface of the emitter. In such a case, the energy distributions may be distorted and structure in them would become more diffuse. In particular, location of both the upper and lower edges of the valence band would become less definite. With evaporated layers of the kind used here, this difficulty does not appear to be prominent. To the extent that it is present, one concludes that the structures discussed in this paper are even more pronounced than shown here and the low-energy tails smaller. In this connection, see footnote 11, Phys. Rev. **84**, 508 (1951); D. B. Zernov and N. M. Politova, Radiotekh. i Elektron. **4**, 84 (1959); N. A. Soboleva, Radiotekh. i Elektron. **4**, 1903 (1959); P. G. Borzyak, P. M. Marshuk, and O. G. Sarbei, Fizika Tverdogo Tela II, 306 (1960).

scattering phenomena are possible when photon energies are as large as 11.3 ev.[9]

In addition to the sparsity of slow electrons, there is reproducible structure in the distribution. For CsI, in Fig. 1, there are peaks at about $V_0 - V = 1.3$ and 2.3 v when $h\nu = 11.3$ ev. These peaks are separated by a clear minimum at about 1.8 v. When $h\nu$ is changed from 11.3 to 10.3 ev, these features shift towards lower energy E by an amount 1 ev, but retain their form as shown in Fig. 2. The range over which this same experiment can be carried out for RbI is smaller than for CsI. However, in Fig. 1, the portions of the curves drawn with a solid line appear to behave in this way.

Distributions for KI, NaI, CsBr, and CsCl are shown in Fig. 3. For the last three compounds, 11.3 ev is not a sufficiently large photon energy to be satisfactory for this experiment. Nevertheless, the results suggest that for photon energies several volts higher, interesting results should be available.

A plausible and simple explanation may be offered for these findings. Structure of this kind in energy distributions can arise from structure in the valence band, which in the iodides is the $5p$ band of the I^- ion. This band has three branches on an E verses k diagram.[10] The density of states may thus show structure as a function of energy in the band. This structure will show up directly in the energy distribution of photoelectrons, provided that the photoelectric emission process is the usual simple one for all pertinent energies. In calling the process simple, we mean that the entire energy of the incident photon is absorbed by a single electron, which migrates to the surface without important loss of energy and escapes into the vacuum. The kinetic energy of the photoelectron after escape is thus directly related to the energy of the intitial state in the following simple way: $E = h\nu - \varphi' - \epsilon$, where φ' is the intrinsic photoelectric threshold energy (the amount by which the upper edge of the valence band lies below the vacuum level), and where ϵ is the energy by which the
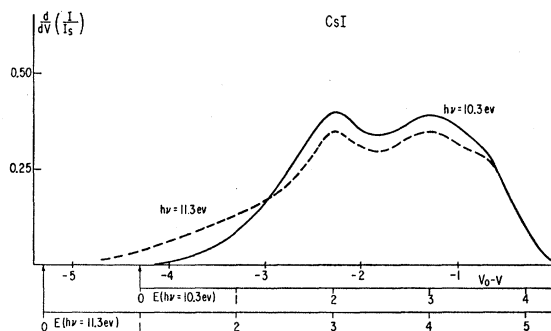

FIG. 2. Energy distributions of intrinsic photoelectrons from CsI for two different values of $h\nu$, 10.3 and 11.3 ev.

[9] L. Apker, E. Taft, and J. Dickey, J. Opt. Soc. Am. **43**, 78 (1953); W. C. Walker and G. L. Weissler, Phys. Rev. **97**, 1178 (1955); E. Taft and L. Apker, J. Opt. Soc. Am. **43**, 81 (1953).

[10] L. P. Howland, Phys. Rev. **109**, 1927 (1958), and cited references. R. G. Cassella, Phys. Rev. **104**, 1260 (1956).

initial state lies below the upper edge of the valence band.

This simple type of process occurs only when the excitation is a one-electron effect and when subsequent scattering of excited electron by valence band electrons is unimportant. The forbidden energy gap in the iodides is about 6 ev. Thus, electron-electron scattering is energetically possible only for incident photon energies above 12 ev. It is obviously ruled out in the present case.

Inelastic scattering of excited electrons by the lattice can occur, but it is a much weaker effect than electron-electron scattering. The photoelectrons emerge from depths of order 10^{-6} cm, which are probably limited mainly by the penetration depth of the incident radiation. In this distance, the energy losses due to lattice scattering apparently do not seriously distort the features attributed here to valence band structure. The low-energy portions of the curves, shown as broken lines in Figs. 1 and 2, are the parts that should be most affected.

In the absence of strong inelastic scattering, then, the energy distributions of photoelectrons show structure that is influenced by structure in the state density of the valence band.

In addition, the photoelectric transition probability will also play an important role, of course, since it may vary as a function of the energy of the initial state. (Figure 2 shows that it is not strongly a function of the excited state.) Structure within the energy distribution may thus be prominently influenced. It seems improbable, however, that the transition probability alone should reduce the energy distribution to the low values observed here over an extensive range of low kinetic energies.[11] Thus, we think that the density of initial states has dropped to very low levels in this range. In other words, the valence band is 3 to 4 ev wide in CsI and RbI.

The experimental data do not at this point give evidence that the bottom of the valence band is as sharply defined as the top. There may be several reasons for this. Even though lattice scattering is weak, it may conceivably contribute to the low level part of the energy distribution shown by the broken lines in the figures. It is also quite possible that there is some scattered radiation of lower photon energy than the desired 11.3 ev, which would give rise to a tail at lower energies. In the present work, this stray radiation was estimated to be less than 5% of the desired photons. With further work to minimize this difficulty, we think that the low-energy tails will become even smaller and that evidence for the bottom of the valence band may be made more definite.

In any event, the present results show that photoelectric methods are of considerable interest for obtaining more information about the width and structure
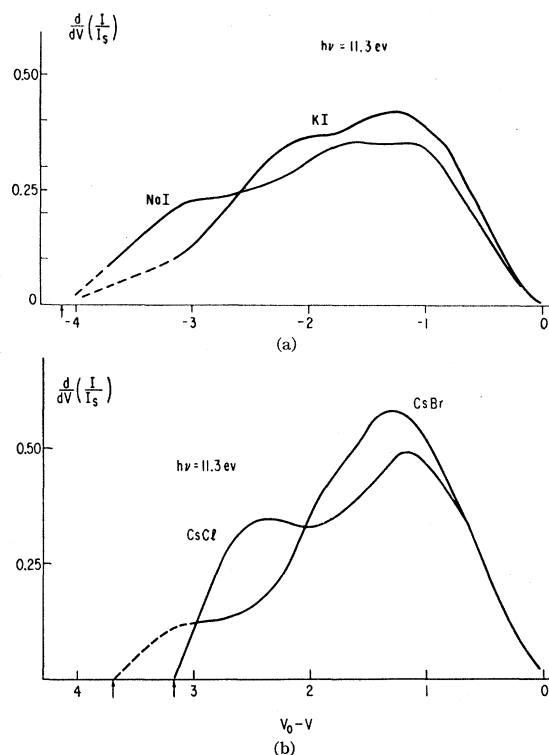

FIG. 3. Energy distributions of intrinsic photoelectrons from KI, NaI, CsBr, and CsCl. Arrows mark the points $V_0 - V = h\nu - \varphi'$ for the respective salts.

of valence bands in crystals like the alkali halides. The important point is that photon energies equal to twice the forbidden band gap are more than sufficient to eject photoelectrons from the bottom of the valence band. The approach furnishes an interesting supplement to soft x-ray emission studies and should be helpful in their interpretation.[12]

More work on the effects described in this paper would be of interest. Photon energies above 11.3 ev would be helpful, and it would be quite feasible to obtain them by eliminating the LiF windows used in this work. At some higher energy, scattering of excited electrons by electrons in the valence band should become important, and the energy distributions should change drastically.[9] For the chlorides and bromides, the present photon energies are inadequate to detect the bottom of the valence band. The photoelectric transitions described here probably involve the participation of phonons (as well as of the surface) in conserving momentum. Hence the results may be weakly temperature dependent, as observed previously for K_3Sb.[13]

ACKNOWLEDGMENT

[11] H. B. Huntington, Phys. Rev. 89, 357 (1953); A. N. Arsenyeva-Heil, *Outer Photoeffect from Semiconductors and Dielectrics* (GITTL, Moscow, 1957), p. 97 (in Russian).

[12] L. G. Parratt and E. L. Jossem, J. Phys. Chem. Solids 2, 67 (1957).
[13] E. A. Taft and H. R. Philipp, Phys. Rev. 115, 1583 (1959); W. E. Spicer, Phys. Rev. 112, 114 (1958).