FAR-ULTRAVIOLET SPECTRA DUE TO $4d$ ELECTRONS IN THE ALKALI IODIDES*

Hiizu Fujita,† Christian Gähwiller, and Frederick C. Brown
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 28 April 1969)

The absorption coefficients of thin films of NaI, KI, and CsI were measured with a grazing-incidence spectrometer in the range 75-250 Å utilizing the synchrotron continuum from the University of Wisconsin 250-MeV electron storage ring. The observed structure is interpreted in terms of both atomic and solid-state effects.

In this paper we present results on the absorption coefficients of thin films of NaI, KI, and CsI in the spectral region 75-250 Å. Detailed structure observed in the range of quantum energies 53 to 60 eV is interpreted as excitation of iodine $4d^{10}$ electrons to p-like final states in the conduction bands. In addition a broad strong resonance is found from 80 to 120 eV and this is identified as the delayed onset of iodine d- to f-like transitions as observed in atomic xenon.[1] The discovery of such atomic phenomena in the solid is important to an understanding of the high-energy optical structure and to the separation of atomic from solid-state effects.

These experiments made use of the 250-MeV high-current electron storage ring at the University of Wisconsin Physical Science Laboratory[2] as a continuum light source. Synchrotron radiation emitted from a small segment of the electron orbit in this machine was focused by a grazing-incidence mirror onto the entrance slits of a 2-m vacuum spectrograph.[3] The samples were mounted in a cryostat before the entrance slits. It was necessary to maintain a vacuum of 10^{-10} to 10^{-9} Torr in that part of the apparatus adjacent to the storage ring, and this was achieved by means of a collimator and ion-pumped separation chamber.

Photon counting was employed in order to permit the use of small slit widths in the spectrometer and a wide range of beam intensities. The detector was an extended cone Channeltron multiplier.[4] A data accumulation system permitted the recording of three channels of information: (1) the signal-counting rate (proportional to transmitted uv intensity), (2) a visible-light monitor (proportional to the incident uv intensity), and (3) the wavelength drum position. This information in digital form was recorded sequentially on tape and processed later at the digital computer laboratory of the University of Illinois.

The samples were evaporated in situ onto thin organic substrates (after first measuring the transmission of the substrates). Lucite, Collodion, and Formvar were each investigated, and Formvar was found to be most suitable because of somewhat better resistance to damage by intense ultraviolet radiation. A quartz-crystal thickness monitor calibrated by the Tolansky method enabled the thickness of the deposited layers to be estimated.

Figure 1 shows the absorption coefficient of the three different iodides at liquid-nitrogen temperature as a function of photon energy. These curves were obtained after correcting for decay of the stored electron beam as well as the measured absorption of the substrate. The absolute value of the absorption coefficients are known to perhaps ±25% whereas the relative densities (or relative absorption constants) are better known. A cell with thin polypropylene windows was installed in the light path so that known rare-gas absorption lines could be used for purposes of

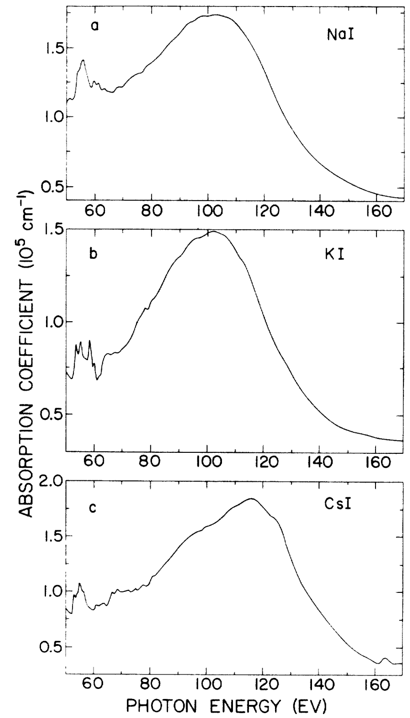

FIG. 1. The absorption coefficient of NaI, KI, and CsI in the range 50-170 eV measured on thin films at 77°K.

wavelength calibration. Tests with He and Xe indicate that the spectral bandwidth for the data of Fig. 1 was of the order of a few tenths of an electron volt.

X-ray emission data[5] indicate that the iodine $4d^{10}$ core ($N_{\mathrm{IV},\mathrm{V}}$ levels) are about 51 to 53 eV deep. Therefore we associate the 55-eV structure[6] seen in all three cases (Fig. 1) with *d* states, unlike the well known ultraviolet exciton spectrum[7] which originates on *p*-like states of the valence band. A detailed scan of the 55-eV region for KI shows a number of lines or singularities which can be grouped in pairs separated by about 1.7 eV. This is close to the calculated[8] spin-orbit splitting of the $4d^{10}$ levels in I^-. The I^- ion has a $4d^{10}5s^26p^6$ configuration and is isoelectronic with atomic Xe and also with Cs^+. In the photoabsorption spectrum of gaseous xenon[9,10] two series of lines separated by about 2 eV are observed between 65 and 70 eV.[11] These series in the gas are due to transitions of the type $4d^{10}5s^25p^6 \rightarrow 4d^95s^25p^6np$, where the first line in each series corresponds to $n = 6$. Sharp transitions to *f* states are not seen in the gas and, in fact, are suppressed because of centrifugal barrier effects.[12]

The prominent lines in KI, especially those at 53.8, 55.5, and 58.6 eV [Fig. 1(b)], increase in height and reduce in width as the temperature is lowered from room to liquid-nitrogen temperature. This suggests that solid-state effects are involved and that the transitions are to *p*-like final states at least associated with the conduction bands of the crystal.[8,13] The detailed band calculations for KI[8] show states with admixture of *p*-wave function beginning at *L* and at *X* points in the Brillouin zone (about 3.5 eV above the lowest minimum at Γ). The width of these "*p* bands" is closely equal to the width (~6.5 eV) of the structure in Fig. 1(b).

In the case of CsI [Fig. 1(c)] the structure seen between 70 and 80 eV is believed to be associated with excitation of $4d^{10}$ states of the Cs^+ ion. Similar structure occurs in the absorption spectrum of CsCl (not shown). Furthermore, an absorption line appears at 164 eV for CsI, and in the range 163-165 eV for the other cesium halides investigated (CsBr and CsCl), which is probably due to excitation of the 4*p* shell of Cs to *s*-like final states.[10]

Perhaps the most important feature of Fig. 1 is the intense broad resonance seen in all three materials extending from 80 to 120 eV. Absorption of this type does not appear for substances such as KBr and KCl; however it is seen shifted to slightly higher energies in CsCl. It is atomic in origin and is due to the delayed setting in of transitions to final states with *f*-like wave function. Such transitions are prominent in the same spectral region for xenon gas as reported by Ederer.[1] These transitions become important well above the suppressed *f* threshold where the final-state continuum wave functions, because of higher kinetic energy, begin to overlap appreciably with the inner 4*d* wave function. Such effects are closely associated with the balance between Coulomb potential and the $l(l+1)/r^2$ term in the radial wave equation for the atom.[14] It is interesting that this effect appears so similar in the gaseous and solid states. This may not be surprising considering the size of crystal field and other solid-state effects compared with the energy of excitation.

Finally, it should be pointed out that the shape of the 80- to 120-eV band is somewhat different in the case of CsI compared with KI or with NaI. This is because some of the oscillator strength on the high-energy side of the broad resonance is associated with delayed *f* transitions from 4*d* states on cesium as well as the iodine.

The authors would like to express their appreciation for the constant interest and help of the staff at the Physical Science Laboratory, especially E. M. Rowe, C. H. Pruett, and F. E. Mills. The suggestions and assistance of A. B. Kunz, R. Z. Bachrach, N. J. Carrera, and W. Scheifley are also gratefully acknowledged.

---

*Work supported in part by the Advanced Research Projects Agency under Contract No. SD-131 and the U. S. Army Research Office, Durham, under Contract No. ARO(D)-217.

†Present address: RCA Research Laboratories, Inc., Machida City, Tokyo, Japan.

[1] D. L. Ederer, Phys. Rev. Letters 13, 760 (1964).

[2] Supported in part by the U. S. Air Force Office of Scientific Research.

[3] Hilger Model No. E580; see A. H. Gabriel, J. R. Swain, and W. A. Waller, J. Sci. Instr. 42, 94 (1965).

[4] Bendix Research Laboratories Division, Southfield, Mich. We are grateful for the suggestions and assistance of Dr. M. Johnson of Bendix Research Laboratories.

[5] Y. Cauchois, J. Phys. Radium 16, 233 (1955).

[6] Our structure for NaI agrees with results recently reported by R. Haensel, C. Kunz, T. Sasaki, and B. Sonntag, Phys. Rev. Letters 20, 1436 (1968).

[7] K. Teegarden and G. Baldini, Phys. Rev. 155, 896 (1967).

[8] A. B. Kunz, Phys. Rev. (to be published).

[9] K. Codling and R. P. Madden, Phys. Rev. Letters 12, 106 (1964).

[10] A. P. Lukirskii, T. M. Zimkina, and I. A. Brytov, Izv. Akad. Nauk SSSR, Ser. Fiz. 28, 772 (1964) [translation: Bull. Acad. Sci. USSR Phys. Ser. 28, 681 (1964)]. The 4*p* to *s* transitions occur at higher energy, 143-145 eV, which we also confirm on measurements of the gas.

[11] At least the first member of each series has recently been observed in solid xenon. See R. Haensel, G. Keitel, C. Kunz, and P. Schreiber, Phys. Rev. Letters 22, 398 (1969).

[12] J. W. Cooper, Phys. Rev. Letters 13, 762 (1964).

[13] Y. Onodera, M. Okazaki, and T. Inui, J. Phys. Soc. Japan 21, 2229 (1966).

[14] U. Fano and J. W. Cooper, Rev. Mod. Phys. 40, 441 (1968).

CHARGE-QUANTIZATION STUDIES USING A TUNNEL CAPACITOR

John Lambe and R. C. Jaklevic
Scientific Laboratory, Ford Motor Company, Dearborn, Michigan 48121

(Received 16 May 1969)

A tunnel capacitor is an array of microscopic resistance-capacitance circuits with the resistive element provided by a tunnel junction. Because of their small size, such microcircuits display special properties due to charge quantization. An array of such circuits shows an oscillatory behavior in its capacitance-versus-voltage measurements. A new type of memory effect is found.

This paper is a report of studies based on a new type of solid-state structure. This structure consists of an array of microscopic series resistance-capacitance elements. The resistance element is formed as a tunneling junction between a metal electrode and a small metal droplet. The capacitance element is formed as a highly insulating oxide between the metal droplet and a second metal electrode. The structure contains a large number of such elements and we call it a tunnel capacitor. This structure makes possible the study of the equilibrium states of microscopic capacitors of such size that the addition of a single electron causes a significant voltage change on one of the capacitors. Thus we can examine the physics of such a system in the case where the quantization of charge becomes an important consideration.

Figure 1(b) shows a schematic representation of this device. It should be noted that it closely resembles a structure which was used by Giaever and Zeller[1] to study zero-bias anomalies in tunneling junctions. There is a very important distinction, however. In their case both oxides were thin enough to permit tunneling since they wished to study tunneling currents flowing between the electrodes. This showed that charge quantization produces a large resistive effect at low applied voltages. The experiments we will describe cannot be carried out unless the second oxide is thick enough to block electron tunneling through it.

Before dealing with experimental methods and results, some of the expected properties of the device will be discussed. Consider an equivalent circuit representing a single element of the array as shown in Fig. 1(a). The tunneling junction is represented by a resistance R and a shunt capacitance C_R. The smaller capacitance C_I is not shunted by any appreciable leakage path. The first quantity we wish to consider is the number of electrons on the metal droplet as a function of the applied voltage V. This question involves a straightforward thermodynamic calculation and the result is sketched in Fig. 1(c). We plot $\langle q \rangle$, the expectation value of added charge, versus the applied voltage V. At $T = 0°\mathrm{K}$, this plot is a set

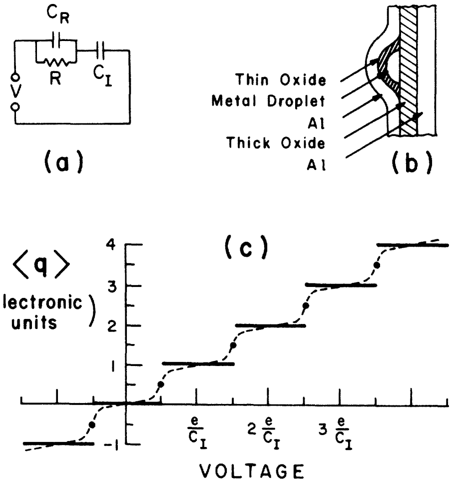

FIG. 1. (a) Schematic of one element of the tunnel capacitor. (b) Structure of the element. (c) Expectation value of added charge on the droplet as a function of the applied voltage V.