# Comparative study of unoccupied electronic states in insulators: CsI

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The results of a comparative study of the unoccupied density of states of CsI by analysis of the inelastic part of the photoelectron spectra, as well as the x-ray-absorption near-edge structure and inverse-photoemission spectra, are presented. It is found that valuable information on unoccupied electronic states in semiconductors or insulators may be obtained from an analysis of the spectral features in the low-kinetic-energy region of photoemission spectra caused by multiply-phonon-scattered electrons.

A detailed knowledge of the unoccupied electronic states is quite important for an improved understanding of a variety of solid-state properties. Recently, a method was proposed to evaluate the conduction-band density of states in semiconductors and insulators, which is based on an analysis of the energy distribution of secondary electrons, observed in the low-kinetic-energy region of photoemission (PE) spectra.[1,2] In the present paper, we report on the application of this method to CsI and compare the results with those of well-established techniques, such as x-ray-absorption near-edge structure (XANES) and inverse photoemission (IPE).

The principle of the new method can be described as follows: Assume an insulator with band gap $E_g$ and a valence-band width $\Delta E_{vb}$ that is smaller than $E_g$ [Fig. 1(a)]. If valence electrons are excited by photons with an energy $h\nu < 2E_g$, the excited electrons cannot scatter with valence electrons, and energy losses are only caused by electron-phonon interaction. Neglecting this interaction, the PE spectrum is expected to consist only of primary excited electrons reflecting in their energy distribution the occupied density of states. In particular, between the vacuum level $E_v$ and the lowest kinetic energy of electrons excited from the bottom of the valence band, $E_{min}$, one would expect a spectral region free of excited electrons. Taking energy-loss processes by electron-phonon interaction into account, multiply scattered electrons will appear in this energy region, with an energy distribution that is intimately related to the unoccupied density of states.[1-4] According to a previously described theoretical model,[1] minima in the intensity distribution of scattered electrons correspond to maxima in the unoccupied density of states, and vice versa.

This can be easily understood in a qualitative way by a simple "golden rule" argument. Assume that the matrix element for electron-phonon interaction is approximately constant and that the energy loss of an electron by a scattering event is negligible as compared to the width of a typical density-of-states feature. Then the scattering
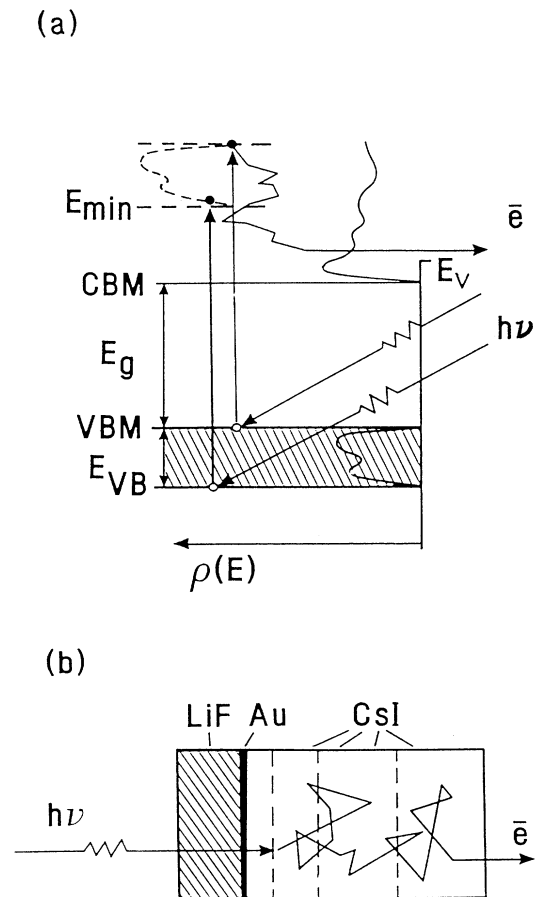


(a)

(b)

FIG. 1. (a) Schematic diagram of the processes underlying the EPSS technique. The density of states in the valence and conduction band of the studied material are given by the solid curves. The dashed curve represents the primary excited PE spectrum, while the zigzag line with arrow indicates a trajectory of a phonon-scattered photoelectron. (b) Semitransparent mode of photoexcitation.

probability $W$ will be proportional to the density of initial states $\rho(E_i)$,

$$W(E_i) \propto (2\pi/\hbar)|\langle f|M|i\rangle|^2 \rho(E_i) \ .$$

Since the probability to find the scattered electron in a state $E_i$ is proportional to $(1-W)$, it will be large for low and small for high density of states.

In order to obtain information on the density of states by the described method, which is called electron-phonon scattering spectroscopy (EPSS) in the following, experiments with CsI were performed. This insulator is particularly suited for such an investigation for the following reasons: (i) the large band gap of CsI, $E_g = 6.2$ eV,[5] establishes the condition for preferential electron-phonon scattering over a wide energy range, (ii) the small electron affinity, $\chi = 0.1$ eV,[5] allows the analysis of the band structure in the region close to the bottom of the conduction band, and (iii) a relatively narrow valence-band width of $\Delta E_{vb} \simeq 2.5$ eV (Ref. 4) gives rise to a wide energy region free of primary excited photoelectrons.

Photoemission spectra of CsI films, taken with 11.6-eV photons from a $H_2$-resonance lamp, are shown in Fig. 2(a). The CsI films were deposited on a gold substrate with thicknesses of 100 (dashed curve) and 2000 Å (solid curve), respectively. The shape of the thin-film spectrum is mainly determined by unscattered photoelectrons reflecting the density of valence-band states.[4] It is clearly seen from Fig. 2(a) that for $d = 100$ Å the energy region $E_v < E < E_{min}$ is rather free of photoelectrons. With increasing film thickness, the scattering efficiency increases, giving rise to additional features $A, C$ (maxima) and $B, D$ (minima) in the low-energy region of the PE spectrum. According to our previous conclusions, these features are related to the density of empty states, i.e., to maxima in the density of states at energies of $\simeq 1.3$ eV (minimum $B$) and $\simeq 2.7$ eV (minimum $D$) above the bottom of the conduction band, $E_{CBM}$ (see Table I), where CBM is the conduction-band mininum. Unfortunately, the presence of nonscattered electrons in this spectrum prevents a quantitative analysis of the density of states, $\rho(E)$, from this inelastic background.

A substantial improvement can be achieved by employing the semitransparent geometry of photoexcitation as described in Fig. 1(b).[2] For this purpose, a thick layer of CsI was deposited onto a transparent LiF window and illuminated from the back. Multiply scattered electrons leave the front of the sample, while contributions of unscattered electrons are strongly attenuated. In this case, the PE spectrum is essentially governed by multiply scattered electrons. Figure 2(c) displays such a PE spectrum of a 900-Å-thick CsI film grown on a LiF substrate with a thin conductive gold interlayer [Fig. 1(b)]. This spectrum exhibits a pronounced structure only in the low-energy region. The energy positions of these features labeled $A_1$, $B_1$, $C_1$, and $D_1$ coincide with those of $A$, $B$, $C$, and $D$ in Fig. 1(a).

The PE spectra of inelastically scattered electrons, taken in the semitransparent excitation mode, were simulated using a solution of the diffusion equation.[1] This results in the energy distribution of multiply-phonon-

scattered electrons as a function of depth in the solid or outside in vacuum for a given density of states, $\rho(E)$. In the present case, the approach was reversed in order to derive $\rho(E)$ from experimental PE spectra. In this way, the density of empty states, $\rho(E)$, shown in Fig. 2(b), was obtained iteratively from a comparison of the calculated and measured curves. Vertical bars in the curve of Fig. 2(b) mark the energies of critical points in the theoretical $E(k)$ dispersion,[6] where one can expect the presence of a high density of states. A more direct comparison of experimental and theoretical $\rho(E)$ curves is not possible due to the lack of a density-of-states calculation for CsI.

In order to check the validity of this correspondence, we performed XANES measurements of CsI at the Cs $N_{III}$ and $M_V$ thresholds using the SX700/II beamline operated by the Freie Universität Berlin at the Berliner Elektronenspeicherring für Synchrotronstrahlung. The
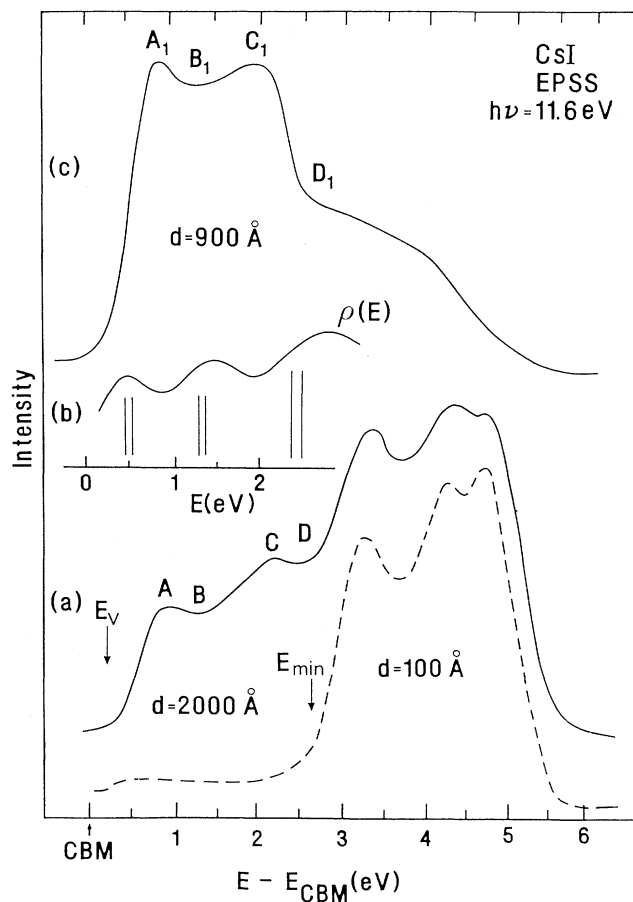


FIG. 2. Results of the EPSS study of CsI: (a) PE spectra for two thicknesses of the CsI film. (c) PE spectrum of a 900-Å-thick CsI film on a transparent LiF substrate, with a thin conductive gold interlayer, taken in the semitransparent excitation mode. The PE spectra were recorded with a total-system resolution of $\simeq 0.15$ eV (FWHM). In (b) the density of unoccupied states $\rho(E)$ obtained from the EPSS study, is compared with the results of a band-structure calculation (Ref. 6).

TABLE I. Energies $E$ and widths $\Delta E$ [full width at half-maximum (FWHM)] of the maxima in the density of unoccupied states derived from the present results in comparison to the positions of critical points in band-structure calculations (Ref. 6). The symmetry character is given in parentheses. All energies are in eV relative to CBM.

| EPSS | | XANES | | IPE | | Theory[a] |
| --- | --- | --- | --- | --- | --- | --- |
| $E$ | $\Delta E$ | $E$ | $\Delta E$ | $E$ | $\Delta E$ | $E$ (symmetry) |
| 0.5 | 0.4 | 0.5 | 0.7 | 0.5 | 0.4 | 0.51; 0.59 $(d)$ |
| 1.3 | 0.6 | 1.2 | 1.0 | 1.5 | 0.7 | 1.10; 1.14 $(d)$ |
| 2.7 | 0.9 | 2.4 | 1.3 | 2.8 | 0.9 | 2.18; 2.29 $(d)$ |
| | | | | 4.7 | 0.6 | 5.47; 5.50 $(f)$ |
| | | | | 6.4 | 1.1 | 5.85; 5.89; 5.91 $(f)$ |
| | | | | | | 5.90 $(d)$ |

[a]Reference 6.

intentions of these XANES studies were (i) to check the validity of the density of unoccupied states derived from the EPSS study in the range of 0–3 eV above the bottom of the conduction band, (ii) to obtain information on $\rho(E)$ at higher energies, and (iii) to determine the orbital character of the final states.

The Cs $N_{\mathrm{III}}$ XANES spectrum $(p_{3/2} \rightarrow d_{3/2}, d_{5/2})$, taken in total-electron-yield mode, is shown in Fig. 3(a). In order to describe the shape of the spectrum, six Lorentzians superimposed on a polynomic background were fitted to the data (solid line and components labeled $a$–$c$, $h$, $g$, and $k$). Since the $N_{\mathrm{III}}$ XANES spectrum should be dominated by transitions from $p$ to $d$ states, the first three intense components $a$, $b$, and $c$ are assigned to transitions into $d$-like states near the bottom of the conduction band. If we identify peak $a$ with transitions into the lowest-lying density-of-states peak observed by EPSS, the relative energy positions of peaks $b$ and $c$ coincide with the other density-of-states maxima obtained from the EPSS study; they are also in good agreement with the results of band-structure calculation, Fig. 3(b). The weak higher-lying structures $h$, $g$, and $k$ coincide in this assignment with transitions into states with mainly $f$ character, which are forbidden by the dipole-selection rule causing the low transition probabilities.

We have also studied the Cs $M_{\mathrm{V}}$ XANES spectrum of CsI $(d_{5/2} \rightarrow f_{5/2}, f_{7/2}$ transitions) in order to verify the origin of the weak higher-lying structures in the Cs $N_{\mathrm{III}}$ XANES spectrum. The resulting spectrum, shown in Fig. 3(c), consists of a dominant broad peak with a weak preedge feature $F$ and a high-energy shoulder $G$. Unfortunately, $f$-$d$ multiplet interaction prevents an evaluation of the data by a simple decomposition into density-of-states features similar to the $N_{\mathrm{III}}$ case. We can only note here, that if we assign the white-line maximum to $f$ states corresponding to peaks $h$, $g$, and $k$ in the Cs $N_{\mathrm{III}}$ spectrum, the preedge feature $F$ corresponds to transitions into lower-lying $d$ states, while the shoulder $G$ can be explained by transitions into mixed $p$-$d$-$f$ states at higher energies [see Fig. 3(b)]. Thus, the $M_{\mathrm{V}}$ results are not in contradiction to the conclusions from the $N_{\mathrm{III}}$-edge studies.

Finally, we have also studied the unoccupied electronic

states in CsI by inverse photoemission, using a spectrometer with tunable photon energy.[7] In order to avoid charging effects, the measurements were performed on thin films of CsI ($d = 30$–$60$ Å) deposited on a Ta substrate, with an electron beam current of only $\simeq 5$ $\mu$A. Such low electron currents caused recording times of $\simeq 4$ h per spectrum. Therefore, the sample was refreshed every two hours by a new CsI deposition in order to avoid surface contamination. A typical spectrum, ob-
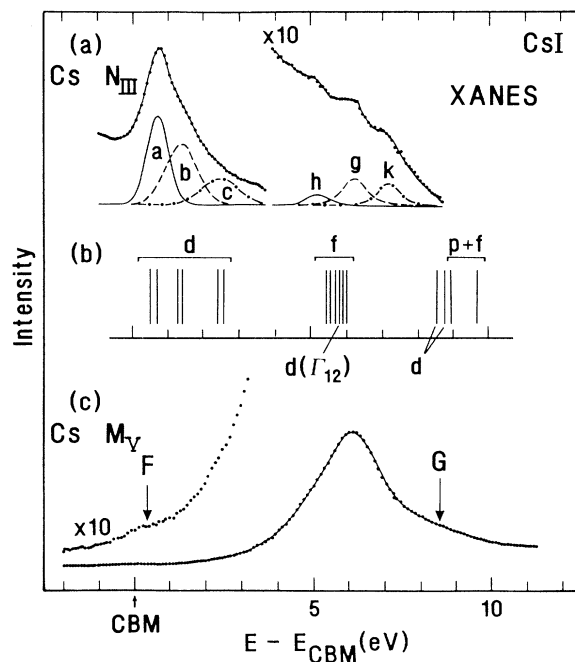


FIG. 3. XANES spectra of CsI taken in total-electron mode: (a) at the Cs $N_{\mathrm{III}}$ (FWHM $\simeq 0.15$ eV) and (b) at the Cs $M_{\mathrm{V}}$ (FWHM $\simeq 0.7$ eV) threshold. In (a), the results of a least-squares-fit analysis are included. The higher-lying region above $N_{\mathrm{III}}$ as well as the preedge region at $M_{\mathrm{V}}$ are displayed with 10 times magnification. The vertical bars in (b) represent the positions of critical points with high $p$-, $d$-, and $f$-like symmetry obtained from the results of a band-structure calculation (Ref. 6).

tained with 22-eV incident electron energy, is displayed in Fig. 4. From a comparison of the experimental data with the results of the band-structure calculation (see above) the $a'$, $b'$, and $c'$ features are assigned to unoccupied states with $d$ character close to CBM, while the features $h'$ and $k'$ most probably reflect tranistions into states with $f$-$d$ hybridized symmetry. The well-resolved $h'$ doublet indicates the presence of the two $f$-derived $E(\mathbf{k})$ branches in the corresponding energy region. Possible Cs $5p$ fluorescence emission, which would also appear in this photon energy region, can be ruled out, since a variation of the energy of primary electrons has no effect on the energy position of these structures relative to $E_F$. The dependence of the position of feature $p'$ on the kinetic energy of the primary electrons, as well as a comparison with the plasmon frequency of CsI,[8] reveal its plasmon origin. The low-energy tail in the spectrum from $-2$ to $0$ eV relative to CBM can be explained by defect states in the band-gap region.

The energy positions of density-of-states features obtained by the different methods as well as the band-structure calculations are summarized in Table I. The presented data reveal a good agreement of the EPSS results with those from XANES and inverse-photoemission spectroscopy. Insignificant deviations of the theoretical values from the experimental ones in the high-energy region may be explained by (i) a possible noncoincidence of the energy positions of band-structure critical points with density-of-states features, (ii) limits of the single-particle approximation underlying theoretical calculations, and (iii) many-body effects and relaxation phenomena in the experimental data. Thus, the presented results indicate the validity of the electron-phonon spectroscopy technique. We hope that the simplicity of the experimental setup for EPSS studies will be useful for future investigations of insulators and semiconductors.
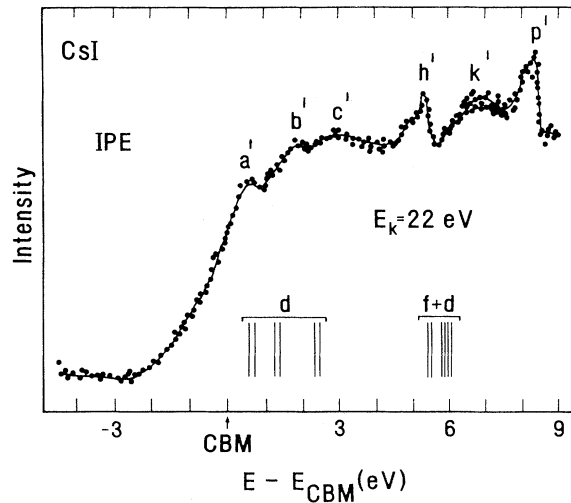


FIG. 4. Inverse photoemission spectrum of CsI taken with a primary electron kinetic energy of $E_k = 22$ eV and a total-system resolution of $\simeq 0.2$ eV (FWHM). The experimental data are again compared with the results of a band-structure calculation (vertical bars) (Ref. 6).

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