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Unoccupied density of states in solid Xe from electron-phonon scattering spectroscopy

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A new geometry for electron-phonon scattering spectroscopy (EPSS) is proposed and applied to study the unoccupied density of states in solid Xe. It makes use of a substrate with a wavelike surface topology to support thick films of the material under study. In this way, EPSS can be applied to the study of wide-gap materials, without the previous limitation concerning the magnitude of the band gap. Experimental results obtained with this method are presented for a thick film of solid Xe and compared with other experimental and theoretical results from the literature.

In the past decade, considerable progress has been made in the study of the unoccupied electronic structure of solids, thin films, and surfaces. There are now a number of well-established experimental techniques, such as optical spectroscopy,[1] inverse photoemission (IPE),[2,3] and x-ray-absorption near-edge structure (XANES) spectroscopy,[4] that have been shown to provide reliable results and can be applied to a large variety of systems. Besides obvious benefits, however, all these methods carry specific disadvantages that justify the search for alternative methods of probing the unoccupied density of states. While optical spectroscopy only provides information on the joint density of states, the use of intense electron beams in IPE can cause problems with charging or decomposition of the sample. Furthermore, the addition of an electron in IPE can result in an energy shift of the observed density-of-states structure with respect to the ground state. In addition, the low photon efficiency in IPE leads to long data-accumulation times that can be prohibitive for materials with high chemical reactivity. XANES spectra, on the other hand, are often difficult to interpret due to core-hole-induced effects.[5]

This situation stimulated the development of alternative methods for the study of unoccupied electronic states, which are based on the analysis of secondary-electron spectra.[6–8] The basis for these methods is the fact that primary electrons, which after excitation pass through the solid, will scatter into empty states with a probability proportional to the unoccupied density of states. Since, on the other hand, electron-electron scattering depends on the occupied density of electronic states, these methods can hardly be applied to the study of metals, where strong electron-electron scattering occurs. In materials with a band gap, E_g, however, electron-electron scattering cannot occur for energy losses smaller than the threshold energy for electron-hole pair creation, E_{th}. This threshold energy varies for different materials over a wide range of energies from $\simeq E_g$ (Ref. 9) up to even $\simeq 3E_g$.[7] For energy losses smaller than E_{th}, however, electron-phonon interaction is the dominant electron-scattering process.[10]

In a recent experiment, the direct observation of the conduction-band density of states of solid Ar by high-resolution electron-energy-loss spectroscopy was accomplished.[8] In this work, energy losses due to single electron-phonon scattering events were observed and analyzed accordingly. A different, but related, approach, which we named electron-phonon scattering spectroscopy (EPSS),[6,10,11] makes use of the low-kinetic-energy region of photoemission (PE) spectra caused by multiple phonon-scattered secondary electrons. In these experiments, a back-side geometry was used, where photoelectrons are excited by photons hitting the back of a sample, so that they arrive at the surface only after a long passage through the sample with the opportunity for many scattering events. This experimental approach is schematically shown in Fig. 1(a). The photon beam passes through a LiF substrate and a thin Au interlayer before reaching the CsI sample and giving rise to photoemitted hot electrons.[6] For thick samples and photon energies smaller than $2E_g$, the electron-emission spectra are completely governed by electron-phonon scattering, and minima in the energy distribution curve are related to maxima in the unoccupied density of states. Even though this method is characterized by a simple experimental setup, it cannot be applied to wide-gap insulators. The reason is that this geometry requires the use of substrates that are transparent for photons with energies up to $\simeq 2E_g$ of the material under study. This means that even the use of LiF as a substrate, with a band gap of $\simeq 12$ eV, will not enable the investigation of insulators with $E_g > 6$ eV.

In the present paper, we report on a geometry for EPSS experiments that eliminates this previous restriction, and allows us to apply this technique to the study of the unoccupied density of states in wide-gap insulators. This geometry is used to study the unoccupied density of states of solid Xe [$E_g = 9.33$ eV (Ref. 12)]. The obtained results are discussed on the basis of the band structure of Xe (Refs. 13 and 14) and are compared with previous experimental results obtained by IPE.[15]

The geometry is schematically shown in Fig. 1(b). The

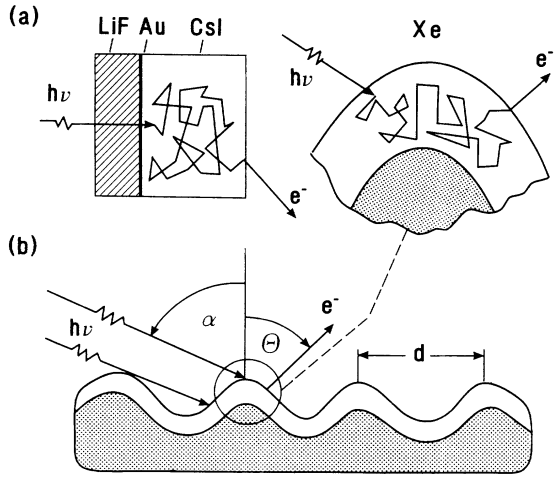

FIG. 1. (a) Schematics of back-side photoemission geometry: The studied insulator (CsI) was deposited on a semitransparent LiF/Au (thin-film) substrate. (b) New geometry for electron-phonon scattering spectroscopy: A sinusoidally profiled substrate ($d=280$ nm) is covered by a thick solid-Xe film. An uv beam at an angle of incidence, α, illuminates only one side of each groove. The angle-resolved PE spectra are obtained from the shadowed surface at an electron-emission angle, θ. A possible electron-transport path in the profiled solid-Xe film is schematically shown in the upper right corner.

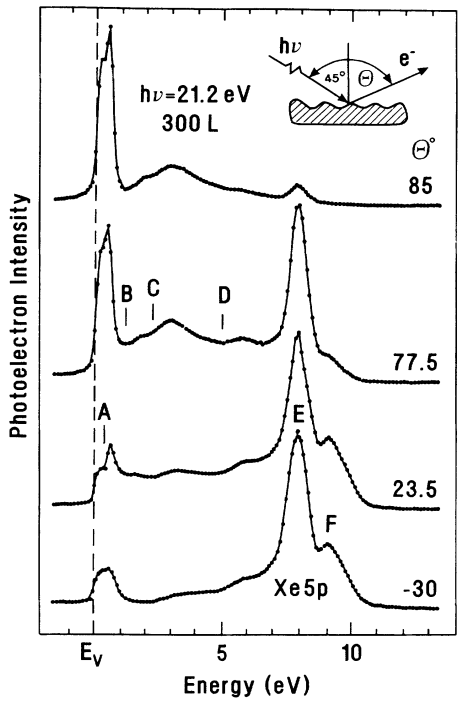

FIG. 2. He I–excited angle-resolved photoemission spectra of a thick solid-Xe film grown on a sinusoidally profiled substrate ($T=30$ K, 300-L Xe). The spectra were taken for a fixed angle of light incidence $\alpha=45°$ and various electron-emission angles θ. The observed minima in the region of secondary electrons are labeled *A*, *B*, *C*, and *D*; the valence-band PE peaks are labeled *E* and *F*.

essential point is that we use an optical grating with a wavelike topology as a substrate for a thick film of the solid under study. In the present work, a dose of 300 L of Xe was deposited on the substrate at a temperature of 30 K in order to produce a sinusoidally profiled polycrystalline Xe film. PE spectra of Xe were measured with a VG-ADES400 electron spectrometer equipped with a He-discharge lamp. The grating was oriented in a way that the He I photon beam at an angle of incidence of 45° illuminates only one side of the grooves. In this way, electrons passing through the thick Xe layer lose their energy by multiple electron-phonon collisions, as indicated in Fig. 1(b). The angle-resolved PE spectra obtained from the shadowed regions of the Xe-covered grooves consist, therefore, mainly of multiple scattered electrons. In order to show the essential role of the wavelike topology of the substrate, corresponding measurements were performed for a Xe film deposited on a flat polished Ta substrate.

He I–excited PE spectra of the thick Xe layer deposited on the sinusoidally profiled substrate are shown in Fig. 2 for various electron-emission angles θ and a constant angle of light incidence, $\alpha=45°$. The spectrum at the bottom of the figure stems from the illuminated surface ($\theta=-30°$), and consists mainly of primary photoelectrons from Xe-$5p_{1/2,3/2}$-derived valence-band states (lines *E* and *F*). The relatively weak intensity of secondary electrons in this spectrum is due to the low efficiency of electron-electron scattering for all primary photoelectrons, with the threshold energy being $E_{th}\simeq 8.3$ eV for Xe.[12,16] A smooth structure in the high-binding-energy side of the spectrum appears due to photoelectrons, which were emitted primarily inside the thick Xe layer and were reflected to the surface by multiple electron-phonon scattering. With increasing angle θ, the relative amount of phonon-scattered electrons increases, and, for grazing electron-emission angles, the spectra are dominated by secondary electrons (see the spectrum for $\theta=85°$). A huge peak close to the vacuum level, E_V, indicates the position of the conduction-band minimum, where further energy losses due to electron scattering are no longer possible.

According to a previously described theoretical model,[11] the structure in the spectrum of secondary electrons is inversely related to the unoccupied density of states. This can be qualitatively understood by assuming that the energy loss of an electron in a scattering event is negligible as compared to the width of a typical density-of-states feature. This means that the final and initial density of states are about the same, so that the scattering probability W, according to the "golden rule," is approximately proportional to the initial density of states. Since the probability for finding a scattered electron in an initial state is proportional to $(1-W)$, we expect a high (or low) intensity of scattered electrons in the region of small (or large) unoccupied density of states. A detailed theoretical treatment of EPSS has been given in Ref. 11.

In Fig. 3, we plot the inverse counting rate of the secondary-electron part of the PE spectrum obtained for an electron-emission angle of $\theta=77.5°$ (middle spectrum) as well as an angle-resolved IPE spectrum (upper spec-

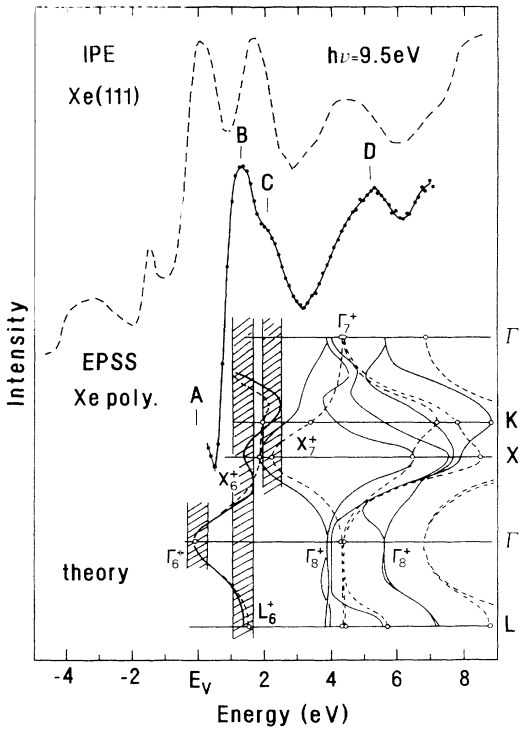

FIG. 3. Comparison of EPSS results for the unoccupied density of states of solid Xe (middle curve with data points) with the results of an IPE experiment (Ref. 15) (top dashed curve); the theoretical band structure of solid Xe from two different calculations [solid bands (Ref. 13) and dashed bands (Ref. 14)] is given schematically in the bottom part of the figure.

trum)[15] and the theoretical band structure of Xe (Refs. 13 and 14) (bottom part of Fig. 3). A comparison shows that the broad maximum D relates mainly to the flat parts and critical points of the dispersion curves along the Γ-L and Γ-K directions. In contrast to the angle-resolved IPE result, the signal around 1.5 eV is resolved into two features, B and C. This is due to the integrated character of EPSS. Due to the large momenta and small energies of phonons, the multiple scattered electrons can occupy any final state independent of symmetry and the value of the $\mathbf{k}$ vector. The EPSS spectrum, therefore, not only reflects dispersing bands around the L point, but also at the X and K points (indicated by the shaded bars). These states are not reached in normal-electron-incidence IPE of ordered Xe(111) films.

The same reason leads to a difference in the shape of feature D between the IPE and the EPSS spectrum. While the rather high density of states around 4 eV, originating at the L point, is emphasized in IPE, it leads to only a shoulder in the EPSS spectrum, where there is also a strong contribution from the density of states at about 5 eV, which comes from extrema in the dispersion curves along Γ-K.

Since PE spectra can only be measured for electrons with kinetic energies above E_V, the low-energy conduction-band density-of-states peak at E_V (electronic states around Γ_6^+ point) is not reliably reproduced in the EPSS spectrum. Shoulder A (Fig. 2) may be attributed to this structure, but the presence of many scattered electrons at the bottom of the conduction band, which cannot be scattered further down by energy loss (intense PE peak close to E_V, Fig. 2), makes the use of EPSS problematic in this energy region.

As predicted by the theoretical model[11] and as can be seen from a comparison with the IPE results and the band structure of solid Xe,[13,14] the EPSS spectrum reflects the unoccupied density of states of solid Xe. Due to electron diffusion over long distances, electron/primary-photohole interaction should not affect EPSS results, in contrast to XANES or PE, where it can lead to energy shifts in the density-of-states features as compared to the ground state. Even though EPSS, certainly, will not replace the established methods, it can serve as a quick analysis tool for the bulk unoccupied density of states of wide-gap materials, with the advantage of employing a comparably simple PE setup.

In order to demonstrate the essential role played by the profiled substrate, we repeated the experiments also with a Xe layer deposited on a flat substrate. Figure 4 displays PE spectra taken from a thick Xe layer grown on a flat polished Ta plate. The spectra obtained for grazing electron emission are totally different from those obtained for the sinusoidally profiled substrate (see Fig. 2); the main difference is in the low-kinetic-energy region. With increasing angle θ, the spectral weights of multiple scattered electrons decrease to almost zero for $\theta = 82.5°$. On the other hand, a new feature G appears, which shifts systematically to higher kinetic energies with increasing θ and also decreases in intensity.

This observation can be easily explained by an escape-cone model. Electrons can only leave a solid if their momentum component normal to the surface is sufficiently large to overcome the surface barrier, E_0. Expressed in terms of the internal electron-impact angle β

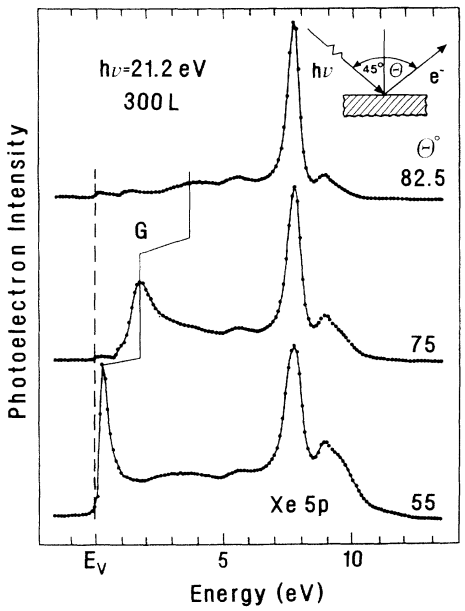

FIG. 4. PE spectra of a solid-Xe film grown on a flat polished Ta substrate. The low-energy cutoff peak is labeled G.

(at which the electron is approaching the surface from the inside), a critical angle β_e will exist for a given kinetic energy E, corresponding to the largest internal electron-impact angle for which an electron of this kinetic energy can escape. This critical angle is given by $\beta_e = \arccos\sqrt{E_0/E}$. Assuming an isotropic distribution of the internal electrons impacting on the surface, the polar-angle distribution of the emitted electrons, $P(\theta)$, is given by $P(\theta) \simeq \cos(\theta)/[E_0/E + (1-E_0/E)\cos^2(\theta)]^{1/2}$. This leads to a cosinelike distribution of the emitted electrons with low kinetic energy ($E \simeq E_0$), while those with high kinetic energy ($E \gg E_0$) will show an almost isotropic distribution. This causes the observed suppression of intensity in the low-kinetic-energy region of the PE spectra for grazing angles.

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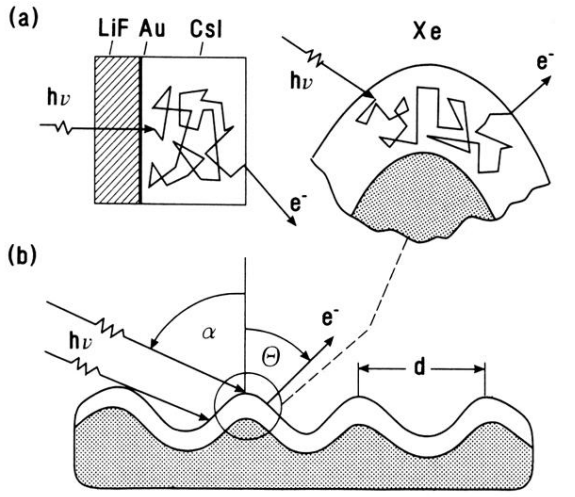

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