# Ultraviolet photoelectron spectroscopy and photoconductivity of CaF$_2$

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Vacuum ultraviolet photoelectron spectroscopy and a systematic study of charging during irradiation with 21.2-eV photons was carried out on cleaved (111) surfaces of CaF$_2$ crystals. The goal was twofold: (1) to find ways of suppressing charging effects and (2) to use surface charging for monitoring photoconductivity. Attempts to reduce charging included crystal heating, use of negatively charged grids at the rear of the sample, and flooding with low-energy electrons. At crystal temperatures between 220 and 350 °C both the negative grid and the flood-gun technique produce charge-free surfaces. The enhanced photoconductivity during UV irradiation is explained by thermally activated diffusion of $V_k$ centers. The observed temperature dependence yields an activation energy of 0.30±0.06 eV. [S0163-1829(97)05612-9]

## I. INTRODUCTION

In this contribution, we report on systematic vacuum ultraviolet (VUV) photoelectron spectroscopy (UPS) studies of cleaved CaF$_2$ single crystals. In view of future investigations of the electronic structure of fluorides in the valence-band region, we tried to develop a technique that allows one to record spectra undisturbed by charging. UPS on insulating samples is generally obscured by charging phenomena causing a shift of peak position, peak broadening, and a distortion of the spectra due to lateral or depth-dependent charge inhomogeneities. For most ionic crystals it is impossible to record meaningful spectra at room temperature since the photoelectrons are retarded by the positive surface charge. In CaF$_2$, however, a conduction mechanism is activated at an elevated temperature that reduces surface charging and allows one to measure photoemission spectra. This fact requires a better understanding of the photoconductivity during irradiation.

The electrical conductivity of CaF$_2$ is exclusively ionic.[1,2] It is related to the motion of fluorine ions and vacancies through the lattice, a process that is only effective at sufficiently high temperatures (>500 °C). Impurities, such as oxygen or rare-earth ions, are known to increase this conductivity,[3–5] as does irradiation with lasers.[6] For the temperature interval 200–300 °C an ionic conductivity of about $10^{-12}$ $(\Omega\,cm)^{-1}$ was reported.[5] When irradiating with 21.2-eV photons we find a much higher conductivity of about $10^{-8}$ $(\Omega\,cm)^{-1}$ in that temperature range. Hence, for VUV photoconductivity an additional charge transport mechanism must come into play, which, however, might differ for different wavelengths. We propose that for 21.2-eV light and elevated temperatures the mobility of $V_k$ centers is responsible for the increased photoconductivity of CaF$_2$. The $V_k$ center consists of a valence-band hole trapped on a pair of adjacent fluorine ions.[1] Its activation energy for migration was determined[7] to be 0.3 eV, which matches well the onset of photoconductivity found in our experiments. The creation of such valence-band holes is readily explained by photoemission without charge compensation.

The following measures for minimizing charging during UPS on insulating samples have been proposed in the literature: One way is heating the crystals, as described by Pong, Paudyal, and Brandt.[8] Activating photoconductivity was applied by Salanek and Zallen,[9] especially to micrometer thin samples, as demonstrated in their work on As$_2$S$_3$ thin films. A third approach to suppress charging during photoemission is to supply compensating charges by flooding the surface with low-energy electrons from an auxiliary electron gun (flood gun) (Ref. 10) or a simple filament. The latter technique was successfully utilized by Himpsel and Steinmann[11] in case of NaCl, while Salaneck and Zallen[9] found no effect on their valence electron spectra of As$_2$S$_3$. When ionic crystals can be grown as epitaxial layers, charging can be avoided by investigating thin films on metal or semiconductor substrates. A number of photoemission experiments conducted on such films have been reported in the literature.[12–19] In the case of CaF$_2$, no charging was observed for film thicknesses below eight F-Ca-F triple layers terminated by a (111) surface.[19]

We investigated surface charging of large single crystals by observing both position and distortion of the valence-band peak, and by comparing our spectra with those obtained for thin films by other authors. We also present an independent way to determine the charge free state by observing the position of the secondary electron cutoff. To control charging, the above-mentioned techniques were applied, and values of the apparent surface potential for the various experimental conditions are presented. In particular, it will be shown that a grid at negative voltage in electrical contact with the rear of the sample leads to spectra free of charging artifacts when used in conjunction with moderate heating of the crystal. It is expected that these observations for CaF$_2$ apply to other insulating materials as well.

## II. EXPERIMENT

Photoemission experiments were performed in a UHV chamber at a base pressure of $3\times10^{-10}$ mbar. Photoelectrons were excited by 21.2-eV light of a He discharge lamp and recorded with a spherical energy analyzer according to the design of Jost.[20] Spectra were taken by applying an accelerating or retarding field to the analyzer, which was operated in all experiments at a constant pass energy of 10 eV. Hence,

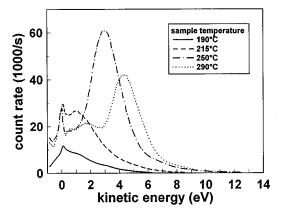FIG. 1. The dependence of VUV photoemission spectra of $CaF_2$ crystals on temperature. No spectrum could be obtained at room temperature.



FIG. 2. Temperature dependence of the change of valence-band peak shifts. The shifts are a measure of the surface potential $U$ caused by charging. The Arrhenius-type plot is based on Eq. (5) defining the quantity $U_0$.

electrons measured at an accelerating voltage of $+10$ V were assumed to have zero kinetic energy. The light source and analyzer were mounted at a fixed angle of 90° with respect to each other and 45° to the surface normal. The chamber was equipped with a low-energy electron source that provided 3–5-eV electrons for flooding the sample. Samples were commercial UV grade $CaF_2$ crystals ($20 \times 20 \times 3$ mm$^3$) from K. Korth Company, Kiel, with (111) surfaces cleaved in air. These crystals were mounted in a copper frame that could be heated up to temperatures of 400 °C. The crystal was electrically insulated from the sample holder by means of thin ceramic plates. In order to apply a potential or to measure the sample current, the back of the crystal was covered by a stainless-steel mesh with separate electrical contact. As an example, during irradiation of a 4-mm$^2$ surface area at 240 °C a chargeup of 2–5 V and a sample current of 2 nA was observed, amounting to a conductivity in the range of $10^{-8}$ $(\Omega$ cm$)^{-1}$. The flux of photons emitted from our discharge lamp was determined to be about $2 \times 10^{11}$ photons/s by measuring the photocurrent of a thin gold foil and correcting for the photoelectric yield of gold.[21] Thus, a quantum yield of 0.06 emitted electrons per incident photon could be determined.

## III. RESULTS AND DISCUSSION

### A. Variation of sample temperature

Initial photoemission experiments with $CaF_2$ crystals performed at room temperature did not give any useful result; i.e., we obtained zero counting rate over the entire range of kinetic energies. Upon heating the sample the valence-band emission emerged. Figure 1 shows photoemission spectra taken at temperatures between 190 °C and 290 °C. At a temperature of 215 °C, a clearly developed valence-band peak appears around 1.5-eV kinetic energy. This peak shifts to higher energies with increasing temperature. At 290 °C the peak position reaches about 4.5 eV, but further heating up to 400° (not shown) still shifts the peak. This peak shift with temperature is clearly related to a positive chargeup of the crystal surface. At room temperature, the ionic conductivity of the crystal is too low to counteract the charge loss due to electron emission. Raising the temperature increases the photoconductivity by mobilizing charge carriers.
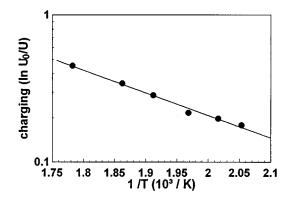
To study this effect in more detail we recorded spectra at various temperatures and extracted the valence-band peak positions. In order to obtain the corresponding surface potentials, we compared these peak positions with the binding energies reported for thin films. In Refs. 13 and 14, the valence-band peak was found at a binding energy of 10 eV, measured with respect to the valence-band maximum of the Si substrate. For film thicknesses beyond two triple layers, the Fermi level was found to be pinned at the Si valence-band maximum.[13] For our spectrometer, the measured kinetic energy of electrons emitted from the Fermi level of silver is 16.4 eV. Therefore, we expect to see the $CaF_2$ valence-band peak for an uncharged surface at a kinetic energy of 6.4 eV, and any deviation of the peak position from this value is interpreted as due to surface charge. Although it has been observed that the position of the bands relative to the Fermi level depends on the stoichiometry of the interface[13,14] or the deposition of material on top of the film,[15] the above interpretation is confirmed by our measurement of the secondary electron cutoff described in Sec. III B, which constitutes an independent check that the surface is uncharged. In Fig. 2 the logarithm of the inverse of these deviations is plotted versus $1/T$. The constant $U_0$ appearing in Fig. 2 is to match the units; its physical significance is explained in Sec. IV. From this Arrhenius-type graph the activation energy of the charge carriers that are responsible for the additional photoconductivity during radiation was found to be $0.30 \pm 0.06$ eV (see also Sec. IV).

In addition to the shift to higher kinetic energies, we observed a growing yield with increasing temperature until the counting rate reaches a maximum at about 250 °C. Spectra taken at higher temperatures again show diminishing peak intensities. This yield variation is presently not well understood. It may be caused by an increased recombination of the charge carriers with increasing temperature. On the other hand, we cannot exclude instrumental effects such as a change in effective acceptance angle due to electron deflection by the electric field variation originating from surface charge.

In another series of measurements we changed the VUV radiation intensity. Figure 3 shows spectra taken at two temperatures with intensities that differed by a factor of 2. The results prove that the peak position does not shift signifi-
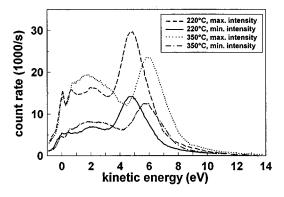
FIG. 3. Photoemission spectra at two sample temperatures for two VUV light intensities differing by a factor of 2.

cantly with light intensity, which means that the surface potential is not affected by intensity. Since in photoconductivity the number of charge carriers is expected to grow proportionally to the light intensity we conclude that the increase of carrier density with intensity leads to a correspondingly larger current flow through the sample, thereby preventing any increase of charging at higher intensities.

### B. Negative grid potential

An attempt was made to change the electric field between sample and spectrometer and counteract the positive surface potential by applying a negative potential to a conducting grid placed in contact with the rear side of the sample. With such an arrangement still no photoelectron spectrum could be observed at room temperature, even at grid voltages as high as $-300$ V. The situation changed again when heating the sample. At temperatures higher than 200 °C we observed a clear shift of the whole spectrum towards higher kinetic energies when applying negative voltages to the grid as illustrated in Fig. 4. The linear relationship between grid voltage and peak position for three temperatures above 200 °C is shown in Fig. 5. The peak position shifts linearly with grid voltage and the slopes of the straight lines as well as the charge at zero grid potential depend on temperature. The horizontal dashed line indicates the peak position for an uncharged surface expected from comparison with thin-film results. Its intersection with the straight line gives the grid voltage that needs to be applied to reach this peak position at a given temperature. For example, at 240 °C $-8$ V are required to compensate the surface charge potential and to record an undisturbed photoemission spectrum.

An independent way to determine the charge free state is the observation of the shift of the low-energy cutoff of the secondary electron peaks as a function of grid voltage, illustrated in Fig. 6. The surface charge is compensated when the secondary electron peak reaches a maximum while the cutoff edge is still at the smallest possible kinetic energy. Figure 6 presents some spectra that served to determine this critical grid potential at a sample temperature of 240 °C. A spectrum taken with a grounded grid at 240 °C (see Fig. 4) does not show the whole secondary electron spectrum since very-low-energy electrons return to the sample surface due to its attractive potential. On the other hand, for a grid potential of $-10$ V the cutoff edge was found at a kinetic energy of about
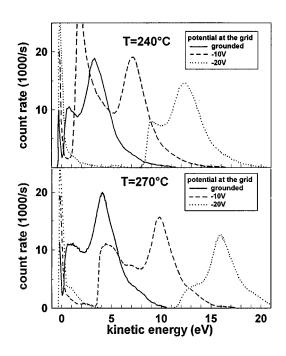


FIG. 4. Valence-band peak positions for different potentials applied to a grid at the rear of the crystal, measured at two temperatures.

1.5 eV, implying that the surface potential was over compensated. From the spectra in Fig. 6 we conclude that a grid voltage of $-8$ V is appropriate for balancing the surface potential due to charging. In this case, the valence band peak is again found at a kinetic energy of about 6.4 eV, consistent with the dashed lines in Fig. 5. Hence, analysis of the secondary electron peak as a function of grid voltage confirms the result obtained by comparison to thin film experiments.

### C. Charge compensation by low energy electrons

With the measures described so far, we tried to counteract surface charging due to photoemission by increasing the charge transport through the crystal. In order to obtain a sufficiently large photoconductivity, it was necessary to work at temperatures higher than 200 °C. However, for some investigations, especially studies of defects, it may be desirable to measure photoemission spectra at lower tempera-
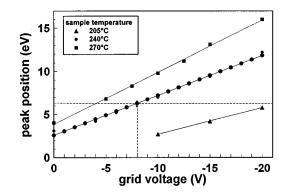


FIG. 5. Shifts of the valence-band peak position with grid potential applied to the rear of the crystal. The slopes are 0.31 eV/V at 205 °C, 0.46 eV/V at 240 °C, and 0.6 eV/V at 270 °C.
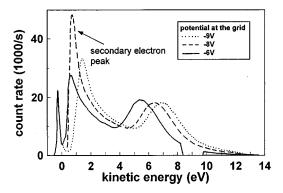
FIG. 6. Use of the secondary electron peak for determining the optimal grid potential, which ensures undisturbed photoemission spectra. The crystal temperature was 240 °C.

FIG. 8. Photoemission spectra taken at different temperatures under identical floodgun conditions (4 eV, medium current).

tures. One way to approach this goal is to flood the surface with low-energy electrons during the photoemission experiment[10] by utilizing an auxiliary electron gun. We tested this technique and showered the sample at room temperature with 4-eV electrons at different current levels. Typical results are shown in Fig. 7. At a sufficiently high neutralizing current it was indeed possible to reduce charging to an extent that the valence-band peak emerges from the elastic peak of the flood-gun electrons. Charge compensation clearly depends on the floodgun current, which can be controlled by taking the integral over the elastic electron peak. However, following this procedure at room temperature, the valence-band peak is strongly broadened compared to the results of higher-temperature measurements. This might be due to depth-dependent inhomogeneities in charging and a buildup of a charge cloud by flood-gun electrons causing inelastic scattering of the photoelectrons. When, however, the photoconduction mechanism is activated by heating the crystal while the flood-gun current remains unchanged, the peak regains its original width as demonstrated in Fig. 8 for medium flood-gun currents. Note that the valence-band peak in the spectrum taken at 250 °C is at a higher kinetic energy compared to the value observed at 350 °C. This indicates that with this flood-gun current at 250 °C charging was overcom-

pensated and the surface gained a negative potential. The conductivity of the crystal, on the other hand, is still too small to remove this negative excess charge in the near surface region. At 350 °C the conductivity seems sufficient to allow the excess charge to flow through the crystal to the grounded grid behind the sample, thereby achieving charge compensation within the total escape depth of the photoelectrons. In this case, the valence-band peak was again found at a kinetic energy of about 6.4 eV.

## IV. CONDUCTION MECHANISM

$CaF_2$ is known to be an ionic conductor, the charge carriers being mainly anti-Frenkel defects,[2] involving equal concentrations of $F^-$ vacancies and $F^-$ interstitials. The activation energy for the formation of this defect has been measured to be 2.2–2.8 eV.[1] The activation energies for migration have been determined to be 0.53–1.64 eV for the anion interstitials and 0.52–0.87 eV for the anion vacancies.[1] Corresponding to these activation energies, Svantner and Mariani[5] determined an ionic conductivity of about $10^{-12}$ $(\Omega \, cm)^{-1}$ at 230 °C for their pure $CaF_2$ samples. In our experiment, the conductivity during VUV irradiation at 240 °C was found to be of the order of $10^{-8}$ $(\Omega \, cm)^{-1}$, i.e., 4 orders of magnitude higher. We propose that this strong enhancement is caused by mobile $V_k$ centers, generated in photoemission. At elevated temperatures these molecular cations remove the positive surface charge generated by photoemission. The activation energy for this motion could be determined to be 0.30 eV (see Fig. 2), in good agreement with values given in the literature.[7,22]

Such an interpretation is based on the fact that within the escape depth of the photoelectrons—which is roughly comparable to the optical penetration depth of the 21.2-eV radiation—photoemission creates holes in the valence band that will not be neutralized by electrons to form self-trapped excitons.[23] Because of the strong electron-lattice coupling in $CaF_2$ these holes will quickly be trapped and stabilize as $V_k$ centers.[24] At elevated temperatures these $V_k$ centers can be thermally activated[22,25] and serve as cations to increase photoconductivity. The large difference between the ionic conductivity[5] and the one we observe during VUV irradiation suggests that the current is due to these photogenerated carriers and in first order independent of interstitial and extrinsic ionic conductivity.
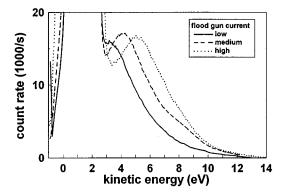
FIG. 7. Photoemission spectra recorded at room temperature while flooding the surface with 4-eV electrons at three different current levels. The counting rate of the elastic peak was used to calibrate the current. The current levels were in units of $10^6$ counts: low: 2.0; medium: 2.6; and high: 3.8.
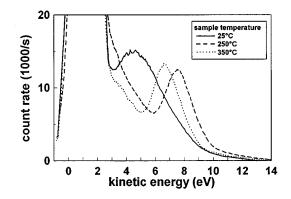
In this work we measured the photoconductivity indirectly via surface charging that shows up as a shift of photoemission peaks. Consequently, the activation energy was derived from the variation of the surface potential with temperature. The connection between photoconductivity $\sigma$ and surface potential $U$ can be made by a simple model based on Ohm's law,

$$\mathbf{j} = \sigma \mathbf{E}, \tag{1}$$

where $j$ is the current through the sample and $E$ the electric field across the sample. The positive charge sheet at the surface—the thickness of which is determined by the escape depth of the photoelectrons—sets up an electric field

$$E = U/\epsilon d \tag{2}$$

across the crystal of thickness $d$. The photoconductivity $\sigma$ can be expressed in terms of the density of holes ($V_k$ centers), $n$, generated in photoemission times their mobility $\mu$,[2,26]

$$\sigma = nq\mu. \tag{3}$$

The thermal activation of the $V_k$ center motion is governed by the Boltzmann distribution, which determines their mobility. Hence, we can write

$$\sigma = nq\mu_0 \exp(-E_a/kT), \tag{4}$$

where $\mu_0$ is the reference mobility at $T \to \infty$. The density of charge carriers, $n$, should be considered as an average quantity, which includes the average lifetime of the $V_k$ centers.

Combining Eqs. (1) through (4) we obtain

$$\frac{U_0}{U} = e^{-E_a/kT}, \tag{5}$$

with

$$U_0 = \frac{\epsilon d}{nq} \frac{j_0}{\mu_0},$$

where $j_0$ is the photoinduced current density at $T \to \infty$. For Eq. (5) to be valid, the ratio $j_0/nq$ must be constant. Since the number of holes generated in photoemission is proportional to the photon flux, a change in intensity causes a corresponding increase in current density.

As can be seen in Fig. 2, Eq. (5) well describes the change of surface potential with temperature. Notice, however, that the measurements covered only a rather narrow interval in the low-temperature regime. This assured that no other charge carriers were thermally activated and only $V_k$ centers originating from photoemission contributed to the photoconductivity. The good agreement of the obtained activation energy with values given in the literature for $V_k$ centers[7,22] confirms our model. It would be desirable, however, to cover a wider temperature interval both for gaining a better accuracy and for reinforcing the model.

## V. CONCLUSIONS

The effects of surface charging in UPS with 21.2-eV photon energy have been studied. Two principles were tested as to their ability to produce undisturbed photoemission spectra. One was to increase the charge transport through the crystal, either by raising the temperature or by applying an external electric field. The other was to compensate the positive surface charge by showering with low-energy electrons. In either case, sample temperatures higher than 200 °C were required for recording meaningful spectra. The optimal way to obtain undisturbed spectra was a combination of heating the sample to 240 °C and applying a potential of −8 V to the rear of the 3-mm-thick crystal.

Surface charging in photoemission was utilized to investigate the enhanced photoconductivity during VUV irradiation. At temperatures above 200 °C we found a strongly enhanced photoconductivity of the order of $10^{-8}$ $(\Omega\,\mathrm{cm})^{-1}$, which we suggest to be caused by thermally activated $V_k$ centers. A simple model was presented to relate the shift of photoemission spectra—which reflect the surface potential—to the photoconductivity. From the temperature dependence of the spectral shifts we obtained an activation energy of $0.30 \pm 0.06$ eV for the $V_k$ centers and a quantum efficiency of 6% for their generation.

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