Nature of Core-Electron Excited States in CaF$_2$ Determined by High-Resolution Absorption and Electron-Emission Studies

T. Tiedje,[a] K. M. Colbow, and D. Rogers

Physics Department, University of British Columbia, Vancouver, British Columbia, Canada

W. Eberhardt

Corporate Research Laboratory, Exxon Research and Engineering Co., Annandale, New Jersey 08801

(Received 22 March 1990)

Combining high-resolution absorption and electron-emission spectra for CaF$_2$, we have investigated the nature of the electronic transitions near the Ca L edge and the F K edge. The presence or absence of spectator and participator lines in the Auger decay of the core-hole excited states is direct spectroscopic evidence which enables us to infer whether or not the final state in the absorption transition is a bound state. Additionally we obtain information about the location of the excited-state electron relative to the ion cores.

PACS numbers: 78.70.Dm

X-ray-absorption spectra in the vicinity of absorption edges are known to be rich in chemical and structural information if they can be interpreted. The importance of absorption spectroscopy as a spectroscopic tool will increase as the resolution and intensity of the tunable sources that are available in the vacuum-ultraviolet and x-ray region improves.[1] In this paper we show, with reference to CaF$_2$, that the electron-emission spectra which result from resonant excitation of individual absorption lines (deexcitation spectra) provide new information that is useful in the interpretation of absorption spectra in solids.

The absorption in CaF$_2$ near the fluorine K edge and Ca L edge have been studied extensively in thin films of CaF$_2$ deposited on silicon.[2,3] The measurements reported in this paper were carried out on CaF$_2$ films about 30 Å thick deposited by evaporation on clean GaAs. Based on photoemission and electron-yield measurements as a function of film thickness we conclude that the CaF$_2$ grows uniformly on the surface and that the films are representative of bulk material. The GaAs(100) substrates were cleaned by thermal desorption of the surface oxide followed by a repetitive sputter-anneal process.[4] The GaAs is important because it provides Ga and As $3d$ photoemission lines which act as internal intensity references for the CaF$_2$ photoelectron spectra.

CaF$_2$ was evaporated from thoroughly outgassed CaF$_2$ powder in a BN crucible, onto a room-temperature substrate. The evaporation was carried out in an evaporation chamber where the pressure was $\leq 2 \times 10^{-8}$ Torr during the evaporation. After evaporation the sample was transferred in UHV into an analysis chamber where it was annealed for one minute at 450°C, as measured by a pyrometer. All the photoelectron spectra were taken with synchrotron radiation at the National Synchrotron Light Source, at beam line U1.[5]

In Fig. 1, we show the electron yield from CaF$_2$ in the vicinity of the Ca L edge. To a good approximation the electron yield is proportional to the absorption. The electron yield is measured with a channel plate placed close to the sample with a retarding potential of 140 V, designed to suppress the primary photoemission events. The Ca L edge in CaF$_2$ is dominated by the Ca $2p$–Ca $3d$, core-to-bound-state transition.[6,7] All of the spectral features in Fig. 1 can be interpreted with reference to the spin-orbit splitting of the $2p$ core hole, the Coulomb and exchange interaction between the $3d$ electron and the $2p$ core hole, and the crystal-field splitting
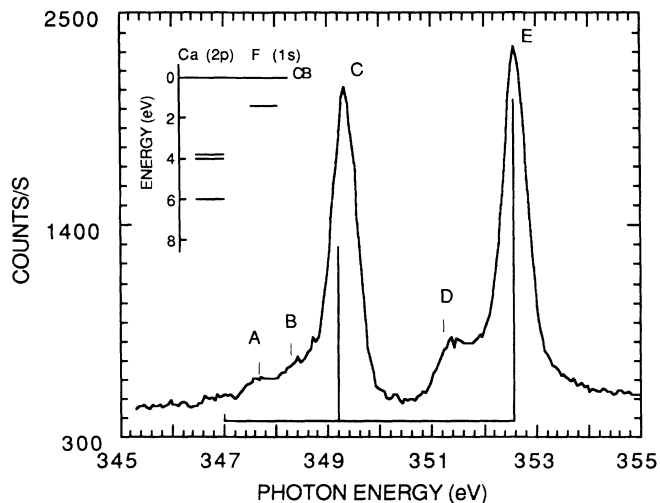

FIG. 1. Electron yield for CaF$_2$ at the Ca L edge with 160-meV resolution, along with a calculated absorption spectrum in which the crystal-field splitting has been neglected. The letters indicate the excitation energies used to obtain the spectra in Fig. 2. Inset: The binding energies for Ca $2p$ and F $1s$ core excitations relative to the conduction band in CaF$_2$. The three Ca $2p$ core-exciton levels correspond to the theoretical spectrum in the figure.

of the $3d$ electron due to the presence of the neighboring fluorine ions, as shown by de Groot et al.,[7] who were able to fit a higher-resolution Ca L-edge spectrum than that reported here using these effects. The calculated absorption spectrum for atomic Ca is shown in Fig. 1.[8] In this calculation we have used the Slater integrals from Ref. 7, a $2p$ spin-orbit splitting of 3.5 eV as determined from photoemission, and we have neglected the crystal-field interaction. This calculation does not show all the spectral features because the crystal-field interaction is not included.

The binding energy of the $3d$ electron relative to the conduction-band edge can be estimated from the energy of the absorption transition, and the energy spacing between the Ca $2p$ core level and the top of the valence band, plus the optical band gap [12.1 eV in CaF_2 (Ref. 9)]. The binding energies of the Ca $2p_{3/2}$ core level and the top of the valence band are 348.9 and 8.0 eV, respectively, in our CaF_2 sample. This results in a binding energy of the $3d$ electron of 3.7 ± 0.2 eV in the final state of the absorption transition C in Fig. 1, if we treat the core hole as a pure $2p_{3/2}$ state. The $3d$ electron in the final state of the transition E has nearly the same binding energy, since the difference in the absorption energy is almost entirely due to the spin-orbit splitting of the $2p$ core hole. The binding energies relative to the conduction-band edge for the three final states of the calculated absorption spectrum in Fig. 1 are shown in the inset. We have treated the core hole for the two lower-energy calculation transitions in Fig. 1 as a pure $2p_{3/2}$ state, and as a pure $2p_{1/2}$ state in the higher-energy transition.

Even though the bottom of the conduction band in CaF_2 has Ca $4s$ character[10] we are able to interpret the absorption spectrum without reference to the Ca $4s$ orbital. A possible explanation is that the relatively weak $Ca\,2p^6 - Ca\,2p^5 4s^1$ transition overlaps with the $3d$ transitions, and cannot be observed separately without a quantitative analysis of the line shapes.

In Fig. 2 we show photoemission spectra for CaF_2 excited at photon energies corresponding to points A–E in Fig. 1. In this experiment the sample is excited with monochromatic radiation and the energy distribution of the photoelectrons is measured. In addition to the Ca $3s,3p$ and F $2s,2p$ core levels, these photoemission spectra show As and Ga $3d$ core levels from the substrate. Also shown in Fig. 2 is the Auger spectrum for CaF_2 excited by broad-spectrum UV radiation centered at 400 eV.

The decay of the core-to-bound-state transitions occurs predominantly ($> 99\%$) via a radiationless Auger process. If the electron which was excited into the bound state in the original absorption event takes part in the transition, the transition is called a participator decay. If, on the other hand, the initially excited electron does not take part in the decay but rather stays around as a spectator, we refer to it as a spectator decay.[11] The par-
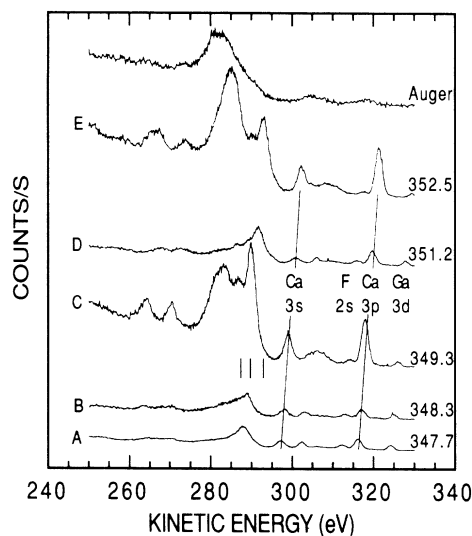

FIG. 2. Photoelectron spectra with 500-meV overall resolution with excitation at a series of different energies in the Ca L edge, corresponding to the points marked with letters in Fig. 1. The spectra are spaced vertically according to the excitation energy, and are normalized to the Ga $3d$ photoemission peak. The three vertical bars below spectrum C correspond to the relative energies of the $1P$, $3P$, and $1D$ configurations of Ca V $(3s^2 3p^4)$.

ticipator decay leads to single-hole final states, which are degenerate in energy with first-order photoemission final states. The spectator decay leads to two-hole, one-electron final states.

The Ca $3s$ and $3p$ photoemission lines in spectra C and E in Fig. 2 are clearly enhanced relative to the F, As, and Ga photoemission lines. We attribute this enhancement to a participator process. Since the final state in the participator process is identical to a photoemission final state, the participator lines are degenerate with normal photoemission lines. The F $2s$ and $2p$ photoemission lines show no participator enhancement, as can be seen with reference to the As and Ga photoemission lines. This confirms that the excitation is localized at the Ca site.

The structure in spectra C and E in Fig. 2 in the vicinity of the main peak in the CaF_2 Auger spectrum is associated with a spectator process. In this process, the bound $3d$ electron remains present to screen the two $3p$ core holes in the final state. This screening lowers the final-state energy so that more kinetic energy is available to the emitted electron. This explains why the spectator lines are on the high-kinetic-energy side of the normal Auger emission. The sharp spectator lines in spectra C and E are almost the same binding energy (photon energy minus kinetic energy) even though the excitation energy differs by 3.2 eV, because most of the difference in energy of the two excitation processes is due to the different angular momentum state of the $2p$ level that is

excited. In spectrum E the higher-energy $J = \frac{1}{2}$ $2p^5$ state is excited while in spectrum C, it is the lower-energy $J = \frac{3}{2}$ state that is primarily excited.

The broader spectral features in spectra C and E, at 283 and 285 eV, respectively, can be attributed to a shakeoff process in which the $3d$ spectator is ionized into the conduction band during the Auger decay. The peak is broadened compared with the spectator lines by the continuum of final states accessible to the ionized spectator. Also, the transition in which the final state is a bare, four-times-ionized Ca ion may have a larger phonon broadening than the transition in which the bound $3d$ spectator electron is present to screen the two $3p$ core holes in the final state. The normal Auger spectrum is broadened, in addition, by the spin-orbit splitting of the $2p$ core hole since the normal Auger spectrum is a superposition of spectra due to the $J = \frac{1}{2}$ and $J = \frac{3}{2}$ core-hole decays. With these broadening mechanisms removed or reduced as they are in the spectator Auger decay, the experimental data suggest that the Coulomb/exchange splitting of the $3p^4$ configuration is resolved. Neglecting the spin-orbit splitting, the $3p^4$ configuration should have three energy levels, corresponding to ^1S, ^1D, and ^3P states. Taking the spacing of these three lines from the $3p^4$ configuration of atomic CaV,[12] we are able to match three spectral features in the spectator spectrum, as indicated next to spectrum C in Fig. 2. In making this comparison we assume that the only effect of the $3d$ spectator electron is to shift the overall spectrum (the spectator model) and accordingly we have shifted the energy scale to match the observed spectrum. Additional contributions to the low-kinetic-energy part of the spectator spectrum could also come from "shakeup" transitions in which the spectator electron is left in a higher-energy bound state such as a $4d$ level after the transition.[13,14]

The two lines between 260 and 275 eV kinetic energy in Fig. 2 correspond to Auger decay processes with a Ca $3s^1 3p^5$ or $3s^0 3p^6$ final state. The sharpness of these lines in spectrum C in particular suggests some spectator contribution in these Auger decays as well. The apparent broadening of these lines in spectrum E can be attributed to the decay of the two $2p$ angular momentum substates, since both are excited in spectrum E.

In light of the spectator-participator processes observed in connection with the Ca core-hole decay we look for similar features at the F K edge. The absorption spectrum of CaF_2 in the vicinity of the F K edge is shown in Fig. 3. This spectrum, like Fig. 1, is obtained in a total-electron-yield measurement, with a retarding potential of 250 V. Although the F K-edge absorption has been measured earlier,[3] it is not understood to the same extent as the Ca L-edge absorption. The F absorption edge is more complicated in that it involves an interatomic transition in which the final-state electron is primarily on the Ca ion.
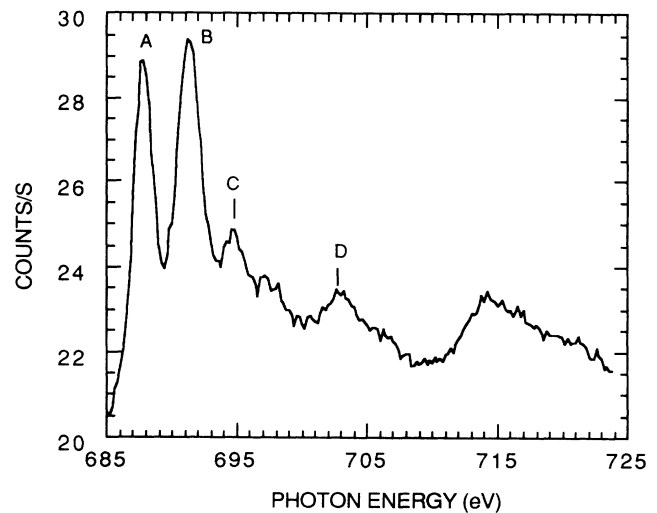
Following a similar procedure to that used for the Ca

FIG. 3. Electron-yield measurement at the F K edge in CaF_2 with 600-meV resolution. The letters indicate the photon energies used to obtain the photoelectron spectra in Fig. 4.

L core excitons, we find that the binding energy of the electron in the state corresponding to the lowest-energy transition (A) in Fig. 3 is 1.5 eV relative to the CaF_2 conduction-band edge, as shown in the inset in Fig. 1. The second peak, B in Fig. 3, involves a transition to a state that lies above the bottom of the conduction band. Since the lower part of the conduction band in CaF_2 is made up of Ca orbitals, with Ca $4s$ at the bottom and Ca $3d$ higher up,[10] the lowest-energy transitions in Fig. 3 must involve interatomic transitions. In this case the high degree of localization of the F $1s$ core hole is likely to have a smaller effect on the binding energy of the F core exciton relative to the valence exciton than it would if the excited electron were on the same atom, as it is in the Ca L edge. In fact, the valence exciton, which consists of a hole in the F $2p$ valence band and an electron in the Ca-like conduction band, has a binding energy of 1.1 eV,[9] quite close to the binding energy of the F $1s$ exciton.

The exciton interpretation for the first peak (A in Fig. 3) is supported by the electron-emission spectrum shown in Fig. 4 obtained by direct excitation of this absorption resonance. All the spectra in Fig. 4 show a clear KLL Auger band near 650 eV kinetic energy. However, only the first spectrum, A, corresponding to the first absorption peak in Fig. 3, shows a distinct spectator line as would be expected if this were the only transition that formed a bound state. This bound state is made up from Ca $4s$ orbitals. We speculate that the next peak, B in Fig. 3, is a Coulomb resonance in the narrow Ca $3d$ bands which lie in the lower part of the conduction band. That is, the Ca $3d$ band is pulled down by the Coulomb attraction of the F $1s$ core hole, but not far enough to form a bound state. In this interpretation the higher-
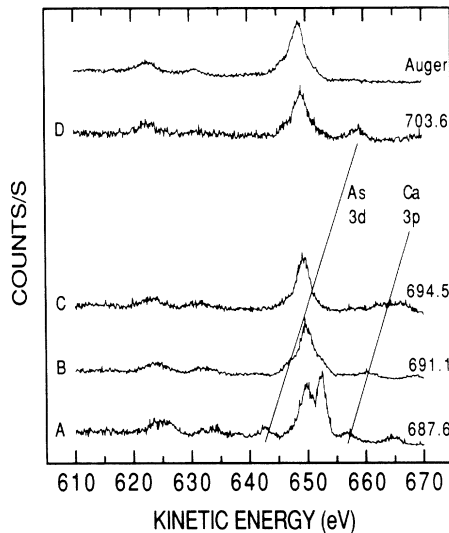
FIG. 4. Photoelectron spectra obtained by excitation at a series of different energies in the F K edge as indicated by the letters in Fig. 3. The spectra are spaced vertically according to the excitation energy, have an overall resolution of 1 eV, and are normalized to the same maximum peak height.

energy spectral features are due to structure in the density of states associated with critical points in the final-state band structure. In Fig. 4 and in other similar data we find no evidence for enhancement in the F photoemission lines that could be attributed to participator processes. This result is consistent with the interatomic nature of the F $1s$ absorption edge. The hole on the F ion has a small overlap with the excited electron on the neighboring Ca ions and hence the probability of a participator decay is small. The other small features in Fig. 4 between 620 and 640 eV are F Auger processes in which the final state has the F $2s^1 2p^5$ configuration rather than $2s^2 2p^4$.

In conclusion, we have measured the Auger decay spectra of the states created by resonant excitation of the Ca L edge and the F K edge in CaF_2. We are able to interpret the new features which appear in the Auger spectra with resonant excitation in terms of a spectator-participator model and obtain new insight into the nature of the fluorine K-edge absorption in CaF_2. The spectator features in the Auger spectra show which absorption transitions have bound final states and the participator lines provide information on the atomic location of the excited-state electrons. Thus the combination of high-resolution absorption and electron-emission spectra has been shown to be a powerful tool to investigate the exact nature of core-electron excited states in ionic compounds.

[a] Also at Electrical Engineering Department.

[1] F. Sette, B. Sinkovic, Y. J. Ma, and C. T. Chen, Phys. Rev. B 39, 11 125 (1989).

[2] D. Rieger, F. J. Himpsel, U. O. Karlsson, F. R. McFeely, J. F. Morar, and J. A. Yarmoff, Phys. Rev. B 34, 7295 (1986).

[3] F. J. Himpsel, U. O. Karlsson, J. F. Morar, D. Rieger, and J. A. Yarmoff, Phys. Rev. Lett. 56, 1497 (1986); C. T. Chen and F. Sette, ibid. 60, 160 (1988); F. J. Himpsel, U. O. Karlsson, J. F. Morar, D. Rieger, and J. A. Yarmoff, ibid. 60, 161 (1988).

[4] S. Sinharoy, R. A. Hoffman, J. H. Rieger, R. F. C. Farrow, and A. J. Noreika, J. Vac. Sci. Technol. A 3, 842 (1985).

[5] M. Sansone, R. Hewitt, W. Eberhardt, and D. Sondericker, Nucl. Instrum. Methods Phys. Res., Sect. A 246, 422 (1988).

[6] J. Barth, F. Gerken, and C. Kunz, Phys. Rev. B 28, 3608 (1983).

[7] F. M. F. de Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky, Phys. Rev. B 41, 928 (1990).

[8] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge Univ. Press, Cambridge, 1959).

[9] G. W. Rubloff, Phys. Rev. B 5, 662 (1972).

[10] R. A. Heaton and Chun C. Lin, Phys. Rev. B 22, 3629 (1980).

[11] W. Eberhardt, E. W. Plummer, C. T. Chen, and W. K. Ford, Aust. J. Phys. 39, 853 (1986).

[12] E. Biémont, Phys. Scr. 34, 318 (1986).

[13] H. Aksela, S. Aksela, H. Pulkkinen, G. M. Bancroft, and K. H. Tan, Phys. Rev. A 37, 1798 (1988).

[14] M. Meyer, E. v. Raven, M. Richter, B. Sonntag, R. D. Cowan, and J. E. Hansen, Phys. Rev. A 39, 4319 (1989).