Soft-X-Ray-Emission Spectra of Solid Kr and Xe

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We present the first soft-x-ray-emission spectra for solid Kr ($4p$-$3d$) and Xe ($5p$-$4d$) that are free of complicating satellite spectra. Monochromatic synchrotron-radiation excitation is used to suppress the satellites. The data are analyzed to determine the $P_{3/2}$ bandwidth for both elements; these results are compared with both photoemission data and available theoretical calculations. Bandwidths are found to be larger than those predicted by most electronic structure calculations.

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Because of their simplicity, rare-gas solids (RGS) have often been used as prototype solids in testing and developing solid-state theory. These gases condense in the fcc lattice and are bonded only by the weak van der Waals forces. There have been some rigorous band-structure calculations performed for these solids [1-6], and some experimental optical [7], photoemission [8-10], and fluorescence [11] studies have provided information about their electronic properties. However, photoemission spectroscopy has been the only technique used in studying the occupied valence-band density of states [8-10]. These studies show significant discrepancies with most calculations. Specifically, the experimentally determined bandwidths exceed the values obtained in almost all band-structure calculations. One explanation is that the band dispersion is simply larger than theoretically predicted [8,9]. Another explanation, proposed by Parrinello *et al.* [12], concluded that the relaxation of the valence-band hole, which exists in the final state of the photoemission process, was the cause of excess broadening seen in the photoemission spectra.

In this paper, we present results obtained from soft-x-ray-emission (SXE) spectroscopy which provide information about the density of states of the occupied valence bands of Kr and Xe. To our knowledge, these are the first SXE measurements on condensed rare gases. We measured $4p$-$3d$ SXE transitions for Kr and $5p$-$4d$ transitions for Xe after the $3d$ or $4d$ core holes had been excited by photons of different energies. As will be seen below, the widths of the upper valence bands of Kr and Xe, namely, the $p_{3/2}$ band, can be determined in a straightforward way from our measurements. Our spectra support photoemission results in the sense that the measured valence bandwidths of Kr and Xe are indeed larger than most theories predict, though the bandwidths we determine differ in detail from those obtained from photoemission.

We note that fluorescence spectra at photon energies of about 10 eV have been extensively studied for the RGS and are found to result from exciton decay [11]. We have looked for, but do not observe, emission at the energy of the core exciton, which is observed in absorption spectra at energies of 91 eV for Kr and 65 eV for Xe [13]. Further, lattice relaxation effects which affect the fluorescence spectra do not play a significant role in our spectra because d core-hole lifetimes (lifetime broadening $\sim$0.1 eV) are much smaller than characteristic lattice relaxation times (phonon bandwidth $\sim$0.006 eV) [14,15].

In rare-gas solids, there is only a small overlap of the wave functions of valence electrons so that the valence bands are narrow and the valence electrons retain much of their local nature. In these circumstances, spectra excited by high-energy photons (or energetic electrons) will have complex satellites associated with localized multiple valence excitations. SXE measurements on gas-phase rare gases [15,16] show strong and complex satellite contributions, which are associated primarily with the excitation of a spectator hole in the valence shell. Similar results are observed in the solid phase. As the spectra below will show, satellites make a prominent contribution to the spectra with high-energy excitation, indicating that the localized nature is retained to a substantial degree in the solid state. However, with selective excitation provided by monochromatized synchrotron radiation, we are able to suppress the satellites and obtain a clean primary spectrum.

Our SXE measurements were performed on beam line U-10A of the National Synchrotron Light Source at Brookhaven National Laboratory. The beam-line monochromator utilizes the e beam of the light source as the input slit, a toroidal focusing mirror, and a normal-incidence transmission grating [17]. With a 1000-line/mm grating, we are able to obtain photons of 4-eV energy bandpass for excitation at 100-eV photon energy. Intensity from higher orders of diffraction and the white-light background are estimated to be less than 15% of the first-order intensity.

Solid Kr and Xe samples were prepared by condensing gases directed onto a graphite substrate which was cooled by a liquid-helium-flow cryostat. The temperature of the cold substrate was around 30 K and the pressure in the sample chamber was roughly 5×10^{-10} Torr during measurements. Condensation was continued far beyond the point where the emission spectra reached its maximum intensity. Macroscopic charging of the sample, which may have a significant influence on photoemission measurements on insulators, does not play a significant role in SXE spectroscopy.

The emission spectra were recorded with a high-efficiency SXE spectrometer [18]. The instrumental resolution is estimated to be 0.1 eV at 80 eV for Kr with a 600-lines/mm grating and 0.18 eV at 55 eV for Xe with a 300-lines/mm grating. The spectra are recorded with a position-sensitive area detector with true photon counting capability.

For insulators with wide band gaps, such as the RGS, there is no overlap between absorption and emission spectra, so that self-absorption will not be a problem in the interpretation of Kr and Xe spectra. Also the spectral broadening due to the lifetime broadening of the valence hole in the final state, which is observed in metals [19] and semiconductors [20], should disappear in the spectra of these large gap insulators, because the nonradiative electronic decay of the valence hole is forbidden energy-wise in this case. The valence hole lifetime in these systems is thus determined by very improbable radiative processes and by electron-phonon processes.

Figure 1 shows solid Kr $M_{4,5}$-$N_{2,3}(4p\text{-}3d)$ emission spectra excited with various photon energies. These spectra show a nearly symmetric peak at approximately 79.9 eV, a high-energy shoulder between 80.4 and 81.6 eV, and a low-energy shoulder extending from 79.0 down to 78.0 eV. These features change very little with increasing photon excitation energy. Another feature at roughly 82.1 eV increases in intensity as the excitation energy is raised, and remains prominent with white-light excitation. In gas-phase SXE spectra [16], similar structures are associated with satellite spectra produced by transitions in atoms with a spectator hole in either 4*s* or 4*p* orbitals. We see very little intensity in that region when the photon excitation energy is at 103 eV, which is below the threshold energy for shakeoff events to occur. The small residual intensity is probably due to the higher-order diffraction of the transmission grating, intrinsic to the monochromator on our beam line. We believe that the emission intensity observed between 78.0 and 82.0 eV in the 103-eV photon-excited spectrum is a clean valence-band emission spectrum without satellite distortion.

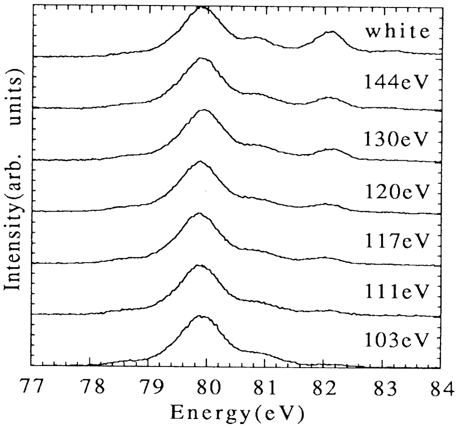

FIG. 1. The solid krypton $M_{4,5}(4p\text{-}3d)$ emission spectra. The excitation energies of the monochromatized synchrotron radiation are indicated above each spectrum; the top spectrum is by white-light excitation.

Figure 2 similarly shows solid Xe $N_{4,5}$-$O_{2,3}(5p\text{-}4d)$ emission spectra excited with photons of different energies. These spectra have a prominent peak at 55.4 eV with a broad feature on its low-energy flank. There is a flat shoulder extending from 56 up to almost 58 eV. The intensity in this region increases with increased excitation energy, and especially with white-light excitation, where it splits into two peaks superimposed on a much higher shoulder. This indicates a strong satellite contribution in this region. However, when we use 70-eV photons with excitation energy below the threshold for valence shakeoff processes, which can produce spectator holes, the emission spectrum still shows intensity in this region, much more than would be produced as satellite intensity by the higher-order diffractions of our monochromator. We believe this is a typical case where satellites overlap the main emission band. We thus will interpret the bottom spectrum in Fig. 2, excited by 70-eV photons, as a primary emission spectrum free of satellites, which extends from 54.0 to 58.0 eV.

In addition to the *d* core-level spin-orbit splittings, the *p* valence bands show a sizable spin-orbit splitting for both Kr and Xe, which varies only slightly from the gas phase, according to the results of Schwentner *et al.* [8]. Thus the dipole selection rule will allow only three transitions for *p*-*d* emission. Figure 3 gives a representation of these three transitions labeled *a*, *b*, and *c*. Since for both Kr and Xe the core-level spin-orbit splitting is larger than the valence-level spin-orbit splitting, transition *a* will be lowest, *b* will be intermediate, and *c* will be highest in energy. Both transitions *a* and *c* come from the $p_{3/2}$ band.

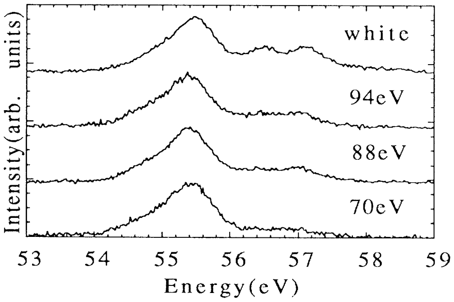

FIG. 2. The solid xenon $N_{4,5}(5p\text{-}4d)$ emission spectra.

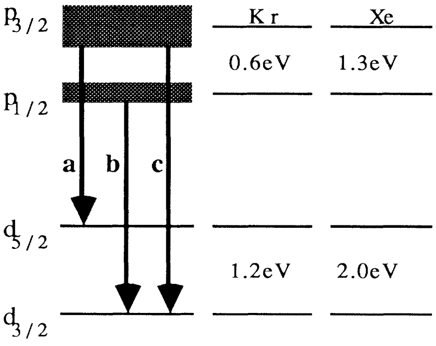

FIG. 3. The diagram transitions under the dipole rule. The numbers indicate the values of spin-orbit splittings of the corresponding levels.

Their centroids should be separated by the core-level spin-orbit splitting, which is 1.2 eV for Kr and 2.0 eV for Xe. Transitions *a* and *c* thus give the lower and upper limits of the $p_{3/2,1/2}$-$d_{5/2,3/2}$ emission range, provided that the lower $p_{1/2}$ valence band, which is the origin of transition *b*, is narrow enough. The centroid of the *b* transition is 0.6 eV from both *a* and *c* for Kr, while it is roughly 0.7 eV from *a* and 1.3 eV from *c* for Xe. All band calculations and Schwentner's photoemission work indicate a much narrower $p_{1/2}$ band than the upper $p_{3/2}$ band. Thus the determination of the width of the $p_{3/2}$ band is straightforward. It will be equal to the difference between the upper emission energy limit defined by transition *c* and the lower limit defined by *a*, minus the spin-orbit splitting of the corresponding core level.

Extrapolation of the bottom spectrum in Fig. 1 gives 78.2 and 81.6 eV for the lower and upper emission edges, respectively, for a total spectral width of 3.4 eV. The extrapolation was done by fitting a straight line with the known broadening parameters of the core lifetime and the instrumental resolution. The spin-orbit splitting for the Kr 3*d* level is 1.2 eV. By the argument in the previous paragraph, this gives the valence $p_{3/2}$ bandwidth of Kr as 2.2 eV. If the $p_{1/2}$ valence bandwidth is substantially smaller than the $p_{3/2}$ width, this result is in substantial agreement with Schwentner's photoemission results, which give a 2.3-eV total *p* bandwidth. Calculations cited below indicate that this is indeed the case. If the $p_{1/2}$ bandwidth is no greater than 1.0 eV and the spin-orbit splitting of the *p* levels is 0.6 eV, a $p_{3/2}$ band of 2.2 eV will extend through the $p_{1/2}$ band and the total bandwidth determined by photoemission will be determined essentially by the $p_{3/2}$ bandwidth. It is obvious from Schwentner's data that the separation of the centroids of the $p_{3/2}$ and $p_{1/2}$ bands are not as pronounced in Kr as in Xe, which is also consistent with this interpretation of the data.

Relativistic calculations of Fowler [1] and Rossler [5] give widths of 0.8 and 0.7 eV, respectively, for the Kr $p_{3/2}$ band, which are considerably smaller than our experimental value. Kunz and Mickish's calculation [3] is nonrelativistic and they obtain a total *p* bandwidth of 1.6 eV. If spin-orbit splitting were taken into account, this calculation would still give too small a value for the $p_{3/2}$ band. Our experimental value is somewhat more compatible with the nonrelativistic band calculated by Lipari [2], who found a 2.8-eV total *p* bandwidth. Clearly, our experimental result for the $p_{3/2}$ bandwidth is larger than all the calculations indicate, except the one by Lipari [2]. Lipari's calculation deserves special attention because it includes many-body electron-correlation effects in the band calculation. The prominence of satellite spectra in our data indicates the localized character of the RGS valence band and strongly suggests that electronic-correlation effects must be taken into account in realistic band calculations for RGS.

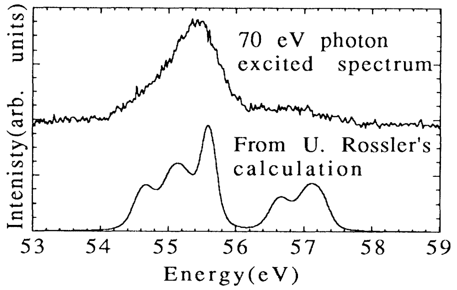

FIG. 4. The comparison of a 70-eV photon-excited Xe $N_{4,5}$ emission spectrum with a spectrum constructed from Rossler's theoretical densities of states.

The data for Xe in Fig. 2 can be analyzed in a similar fashion. From the 70-eV spectrum, we obtain an energy of 54.1 for the lower and 57.8 eV for the upper emission limit, for a total spectral width of 3.7 eV. Subtracting the 2.0-eV *d*-level spin-orbit splitting, we obtain a 1.7-eV width for the Xe $p_{3/2}$ band. Relativistic calculations by Reilly [4] and Rossler [5] give similar values of 0.8 and 0.9 eV, respectively, for the $p_{3/2}$ bandwidth. Both values are significantly smaller than our value. Schwentner's photoemission work [8] gives a total *p* bandwidth of 3 eV and the spin-polarized photoemission performed by Kessler *et al.* [10] gives a similar result. Our $p_{3/2}$ width of 1.7 eV significantly exceeds theoretical values. It is smaller than the photoemission results, but the difference may be attributed primarily to the large spin-orbit splitting of the *p* states in Xe (1.3 eV).

In Fig. 4, we compare the Xe spectrum with a spectrum constructed by convoluting Rossler's calculated density of states (Fig. 2 of Ref. [8]) with the known broadening factors. We adopt the 4*d* core-level binding energies of 67.5 and 69.5 eV, and the centroid of the $p_{3/2}$ band at 12.1 eV from Cardona and Ley [21]. We obtain three x-ray transitions with the intensity modulated by the statistical ratio of the core level. After adding together these three transitions, the spectrum was folded with a Lorentzian corresponding to the core lifetime broadening of 0.1 eV [14] and a Gaussian corresponding to our spectrometer resolution. The spectrum is also multiplied by an ω^3 frequency factor which appears in the one-electron theory of SXE spectra before comparing with the experimental curve, which is the 70-eV photon-excited Xe emission spectrum. The constructed spectrum qualitatively matches the spectral features of the measured one, except that it produces a narrower total spectral width of *d-p* transitions (3 eV compared to our experimental value of 3.7 eV).

These comparisons with theory have meaning only if the SXE spectra accurately represent the ground-state density of states derived from band theory. Two known sources of spectral broadening, lifetime broadening of the core hole and instrumental broadening, have already been accounted for. As noted above, dynamic phonon broadening due to the lattice relaxation about the core hole is suppressed by the short core-hole lifetime. Static phonon broadening of the core level due to fluctuating potentials at a central atom produced by vibrations of neighbor atoms is estimated to be less than 0.1 eV from a simple harmonic-oscillator model of the RGS.

There remains the question of what the SXE spectra represent. A large body of experimental data for metals and semiconductors and more limited work on insulators suggest that the "final-state rule" may be used to interpret emission spectra, though a detailed theoretical justification is available, to our knowledge, only for nearly-free-electron metals [22]. This rule implies that the emission spectra should be compared with a density of states calculated with a filled core hole. If valid, the role of the valence hole, which remains in the final state of the SXE transition, must still be considered.

As noted previously, lifetime broadening of the valence hole will be greatly suppressed in the RGS where the nonradiative electron-electron hole decay processes are largely suppressed. Parrinello *et al.* have argued that an electronic relaxation process related to excitonic shielding of the valence hole is responsible for the broadening observed in photoemission spectra [12]. If present, this effect should equally broaden SXE spectra, since SXE transitions have the same final state as photoemission, but a different initial state. In contrast, studies on simple metals suggest that electronic relaxation processes narrow the spectrum rather than broaden it [23].

Ultimately, we cannot make a definitive choice between three possibilities. (1) The calculated bandwidths of the RGS are too small. Lipari's results suggest that this may result from neglect of correlation effects. (2) The final-state rule does not apply to RGS. The similarity of SXE and photoemission spectra, resulting from processes with the same final state, but different initial states, suggests that this possibility is the least likely of the three. (3) Electronic relaxation about the valence hole in the final state broadens the observed spectra, as suggested by Parrinello.

We hope that the results presented here will stimulate renewed theoretical work on the RGS, which has been dormant for more than a decade. We believe that theoretical efforts to resolve this issue would not only improve our understanding of the spectra of the RGS, but would contribute to the understanding of other solid insulators with highly localized orbitals.

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