

## Evidence for $[1s2p]3p$ shake-up channels in compounds and oxides of third-period elements

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X-ray photoemission spectra (XPS) of NaF, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, InP, and NaH<sub>2</sub>PO<sub>4</sub> collected using synchrotron radiation in the 1900–3400-eV energy range are reported. Accurate XPS spectra have been collected around the Na, Mg, Al, Si, and P 1s photoemission peaks including a region extending for a few hundred eV on the high-binding-energy side. Clear features associated with additional excitations of 2p electrons, more evident in low-Z elements, have been identified. The fine structure of these satellites, dominated by the lower-upper splitting, has been studied in different compounds as a function of the photon energy. Energy positions and splitting are consistent with theoretical predictions. [S0163-1829(96)05523-3]

### I. INTRODUCTION

Satellites of core-level peaks in x-ray photoemission spectroscopy (XPS) have been widely studied, especially in gas phase experiments.<sup>1</sup> The deepest core levels that can be investigated are limited by the energy of the excitation source. In the case of laboratory XPS facilities, equipped with an Al  $K\alpha$  source, 1s core levels can be investigated up to the Mg atom. Photoemission experiments with synchrotron radiation are usually performed using lower-energy sources in the range of grating monochromators. The advent of third generation sources and the development and improved performance of insertion devices are making available intense monochromatized beams suitable for high-energy photoemission experiments. A renewed interest has consequently developed in the possibility to perform photoemission experiments probing inner-shell processes stimulated by deep-core excitations.

A large number of recent x-ray absorption spectroscopy (XAS) experiments indicate that for energies higher than inner-shell absorption thresholds many additional absorption channels open up that are associated with shake-up and shake-off of less bound electrons. The features observed in absorption spectroscopy are sometimes located several hundred eV above the main edge. In particular several clear features have been detected above the  $K$  edge of heavy third-period elements such as in SiX<sub>4</sub> compounds<sup>2</sup> and P, S, and Cl salts.<sup>3</sup> The strongest XAS features are found to be associated with discrete autoionizing resonances resulting from the simultaneous excitation of 1s and 2p electrons to the lowest unoccupied  $p$ -symmetry level. These resonances, corresponding to the threshold of  $KL$  excitations, are exceptionally strong in ClO<sub>4</sub> salts.<sup>3,4</sup> It is expected that by tuning the

photon energy above this threshold, shake-up final states, in which one electron is excited to continuum and the other promoted to the unoccupied discrete level, should be accessible. The effect of these channels in XAS is the increase of the background absorption level through the threshold.

In photoemission spectra shake-up excitation channels are associated with satellite peaks, which provide direct evidence for the existence of these transitions. These are expected to be visible on the high-binding-energy side of main core-level peaks. Shake-off continua should also be visible as a photoelectron background continua. The study of energy intensity and shape of these satellites brings additional insight to inner-shell electron interaction and correlation as well as to the nature of localized excitonic states of selected symmetry to which the shake-up transition can occur.

Very few studies of high-energy core-level peak satellites exist. Neon has been the most widely studied element and a very complex sequence of 1s shake-up satellites has been observed on top of progressively opening shake-off continua. Early investigations<sup>5,6</sup> have been followed by more recent high-resolution low-noise experiments<sup>7,8</sup> that evidenced fine details and line shapes.<sup>8</sup> The problem of the excitation energy dependence of Ne 1s satellites has been addressed and synchrotron radiation experiments with tunable photon sources performed.<sup>9</sup>

The possibility to reveal similar satellite peaks in solid systems has been only recently considered and experiments were carried out with laboratory equipments on Na (Refs. 10 and 11) and Mg (Ref. 12) compounds only. The XPS spectra of Na halides excited by both Mg and Al  $K\alpha$  sources clearly present shake-up satellites corresponding to the excitation of 2p electrons to the 3p level of Na<sup>+</sup> with the typical lower-upper splitting<sup>10,11</sup> as well as of 2s electrons to 3s levels.<sup>11</sup>

The attempt to reveal similar features in Mg compounds such as MgO and MgF<sub>2</sub> has been successful<sup>12</sup> but the presence of a strong tail of secondary electrons prevented the authors from obtaining reliable information on peak profiles. These findings have clearly shown the existence and detectability of high-energy satellite features in XPS spectra of condensed matter. In this paper we present the result of an XPS experiment on several compounds of third-period elements performed using a tunable photon source in the 1880–4300-eV range.

The paper is organized as follows: Experimental details are reported in Sec. II while the results in Sec. III are subdivided into a global presentation of the principal data and specific subsections for increasing atomic number from Na to P. Section IV reports and summarizes the major results and addresses general scientific interest.

## II. EXPERIMENTAL DETAILS

The experiment was performed at Stanford Synchrotron Radiation Laboratory on beamline SB3-3 (Ref. 13) during dedicated beamtime. The SPEAR storage ring was operating at 3 GeV with typical currents in the 50–100-mA range. The Jumbo monochromator<sup>13,14</sup> was equipped with a pair of Ge(111) crystals having a full width at half maximum (FWHM) resolution of about 1.5 eV in the energy range of the experiment. The UHV chamber, commonly used for surface physics experiments, was operating with a base pressure of  $2 \times 10^{-11}$  torr. Photoelectrons were detected with a double-pass cylindrical mirror analyzer used in the constant  $\delta E$  mode with a pass energy of 100 or 200 eV. The overall energy resolution in the photoelectron spectra was in the range 2–6 eV FWHM.

Samples were chosen among UHV compatible oxides or halides of third-period elements. In particular we measured NaF microcrystalline powder, a MgO single crystal cleaved in vacuum along the (100) surface, an Al<sub>2</sub>O<sub>3</sub> single crystal, a SiO<sub>2</sub> single crystal cut along the (10 $\bar{1}$ 0) surface, an InP single crystal cleaved in vacuum along the (111) surface, and a hot sintered pellet of NaH<sub>2</sub>PO<sub>4</sub> salt. For all the insulating samples, charging and peak shifting were avoided using a flood gun, with typical currents of 0.5 mA at 4 V.

The counting statistics required several hours of acquisition per spectrum to evidence the satellite features above the background. The tunable photon source was essential to shift the kinetic energy of the outgoing electrons, to optimize the contrast, and to distinguish photoelectron features from Auger peaks. Particular care has been used in choosing sample holder materials and photon energy to avoid spurious core levels or Auger peaks in the recorded range.

## III. RESULTS AND DISCUSSION

The major results of the present research are summarized in Fig. 1. Typical spectra for NaF, MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and NaH<sub>2</sub>PO<sub>4</sub> recorded at different photon energies are reported. The photoelectron spectra include the 1s core-level peaks (of Na, Mg, Al, Si, and P, respectively) that are aligned on a common additional binding-energy scale  $\Delta E_b$  [for each 1s peak  $\Delta E_b(1s)=0$ ], and are extended to several tens of eV on the high-binding-energy side. On the left-hand side of

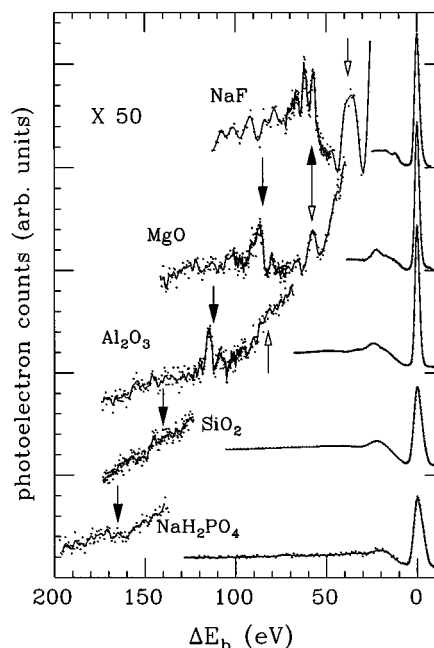


FIG. 1. Typical 1s photoelectron spectra of light third-period element compounds. From top to bottom the spectra refer to NaF at  $E_\gamma=2500$  eV, MgO at  $E_\gamma=2400$  eV, Al<sub>2</sub>O<sub>3</sub> at  $E_\gamma=2500$  eV, SiO<sub>2</sub> at  $E_\gamma=3300$  eV, and NaH<sub>2</sub>PO<sub>4</sub> at  $E_\gamma=3400$  eV. The energy scale  $\Delta E_b$  represents the additional binding energy with respect to the corresponding 1s peak. Relative amplitudes are normalized to the 1s peak area. The shake-up satellite region on the left-hand side is magnified 50 times. The 2p shake-up satellites (dark arrows) and some 2p loss features (light arrows) are clearly visible. The regular trend in increasing  $\Delta E_b$  with Z is quite evident.

Fig. 1 the energy region of the shake-up satellites is reported on a magnified scale to evidence the weak satellite features. The spectra are normalized to the area under the 1s peak and the shake-up region is magnified by a factor of 50.

Several interesting features are visible in Fig. 1. The region between 10 and 30 eV left of the 1s peak is characterized by a visible hump associated with valence-band electron excitations. This feature contains both loss (extrinsic) processes and shake (intrinsic) features that are not separated in energy. In the NaF case it has been the subject of previous studies.<sup>15</sup>

More interesting for the present investigation is the magnified high-energy satellite region. The dots represent the actual experimental points, while the solid line is only a smoothed guide for the eye. All spectra present satellite features in the energy region expected for the 2p excitation with a clear trend as a function of the atomic number Z.

We recall that two different excitations of 2p electrons can be observed and recorded on these spectra of solid-state samples.<sup>10,11</sup> The first is due to a loss process occurring on a 1s peak photoelectron while traveling in the solid that excites a 2p electron of another atom. The corresponding feature occurs roughly at the energy  $\Delta E_b = E_{2p}$  where  $E_{2p}$  is the 2p binding energy. This is an extrinsic process. The other and more interesting process is intrinsic and occurs when a single photon excites simultaneously, on the same atom, a 1s and a 2p electron. This is possible due to electron interaction and correlation. The interaction between the two re-

TABLE I. Binding-energy difference and intensity ratio of the main  $2p$  shake-up satellites in NaF, MgO,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{NaH}_2\text{PO}_4$  compounds with respect to the corresponding  $1s$  peak. The splitting between lower and upper components is reported in the last column. Estimated errors on the last digit are quoted in parentheses.

Element	Compound	Lower peak		Upper peak		Splitting (eV)
		$\Delta E_b$ (eV)	$I/I_{1s}$	$\Delta E_b$ (eV)	$I/I_{1s}$	
Na	NaF	57.2(2)	0.008(1)	61.9(2)	0.010(1)	4.7(3)
Mg	MgO	80.0(3)	0.002(1)	86.0(3)	0.008(2) <sup>a</sup>	6.0(5)
Al	$\text{Al}_2\text{O}_3$	108.5(4)	0.002(1)	114.8(2)	0.006(1)	6.3(2)
Si	$\text{SiO}_2$			145.4(5)	<0.003	
P	$\text{NaH}_2\text{PO}_4$	164.5(5)		173.0(5)	$\sim 0.002$	8.0(6)

<sup>a</sup>Refers only to main component.

sulting core holes requires a higher excitation energy for the process than simply the sum of the two  $1s$  and  $2p$  binding energies. Actually the required energy can be roughly estimated in the  $Z+1$  approximation to be the sum of the binding energy of the  $1s$  plus that of the  $2p$  in the  $Z+1$  atom. Due to the large exchange interaction between the  $1s$  and  $2p$  core holes an observable triplet-singlet (lower-upper) splitting of the main features of a few eV is predicted.

All these features are nicely revealed by the present experiment. Most evident in Fig. 1 are the shake-up satellite features centered around  $\delta E_b = 60$  eV for Na, 85 eV for Mg, 110 eV for Al, 145 eV for Si, and 170 eV for P, with position roughly indicated by the dark arrows. Their relative intensity with respect to the  $1s$  peak reduces progressively as  $Z$  increases. The split lower and upper components are clearly visible in Na, but also in Mg, Al, and perhaps P. Clearly visible are also the  $2p$  loss features in Na, Mg, and Al (broad) as indicated by the small white arrows. It is interesting to note that, as expected from the  $Z+1$  picture, shake-up features in Na and Mg are roughly centered, on the  $\Delta E_b$  scale, on the loss features of Mg and Al.

Due to the smaller cross sections and lower resolution the shake-up peaks in  $\text{SiO}_2$  and  $\text{NaH}_2\text{PO}_4$  are not as evident as in the other compounds; in any case the evidence for their presence is very strong. However, further experiments will be required to provide an unambiguous picture.

The energy positions of the main shake-up features and their relative intensity with respect to the  $1s$  peak are summarized in Table I. The specific results for each element and the whole set of measurements at different energies are discussed separately in the following subsections.

### A. NaF

NaF and various other Na halides were widely studied with laboratory equipment.<sup>10,11</sup> The results of the present experiment are important for the tunability of the photon source but they are not able to add new insight into shape and composition of the satellite features. Actually the use of an Al  $K\alpha$  source combined with multichannel electron detection<sup>11</sup> provides higher counting rates and allowed us to obtain evidence for the complete  $2p$  and  $2s$  shake-up regions.

Photoelectron spectra of NaF have been collected at  $E_\gamma = 1970$ , 2500, and 3040 eV. These spectra are reported and compared in Fig. 2 on the same binding energy  $E_b = E_\gamma - E_{\text{kin}}$  scale. No correction for the work function has

been applied, but in any case the exact peak position is also dependent on flood current and therefore the absolute position is not reliable. The spectra are normalized to the area under the respective  $1s$  peak reported on the right-hand side of the figure. The shift on the ordinate scale is only for graphical purposes. The high-binding-energy region is magnified 100 times. The peak FWHM resulted in 2.94, 3.07, and 3.45 eV, respectively, for the three spectra in order of increasing  $E_\gamma$ .

Several features can be recognized easily. The broad peak centered around 1115 eV is associated with the  $2p$  loss processes. The  $2p$  lower and upper shake-up peaks are also clearly visible around  $E_b = 1135 - 1140$  eV. Additional binding energy with respect to the  $1s$  peak, intensity ratios, and splitting are reported in Table I. They are in relatively good agreement with previous results on Na halides obtained with a laboratory source.<sup>11</sup>

The presence of a background step on the high-binding-energy side of the shake-up doublet is consistently shown by all spectra. It is probably a signature of the shake-off continuum, easily revealed, for instance, in Ne,<sup>7</sup> but, due to the solid nature of the sample, it can also be an artifact of the increased secondary electron background. Finally, weak features, systematically revealed around  $E_b = 1160 - 1170$  eV, are to be associated with the  $2s$  shake-up region. The counting statistics are, however, not sufficient to identify shapes

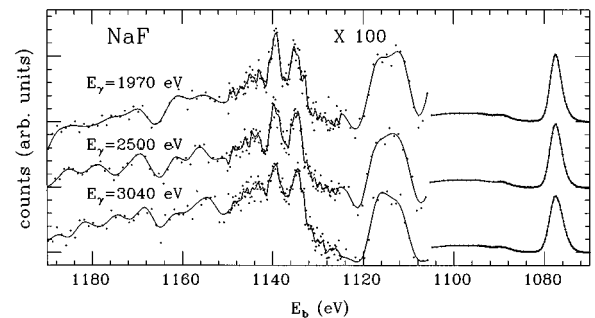


FIG. 2. Photoelectron spectra of NaF as a function of photon energy; from top to bottom the photon energies refer to 1970, 2500, and 3040 eV.  $2p$  loss features at  $E_b \sim 1115$  eV and the nicely split  $2p$  shake-up satellites at  $E_b \sim 1134 - 40$  eV are clearly visible. The feature at  $E_b \sim 1165$  eV should be associated with the  $2s$  shake-up region.

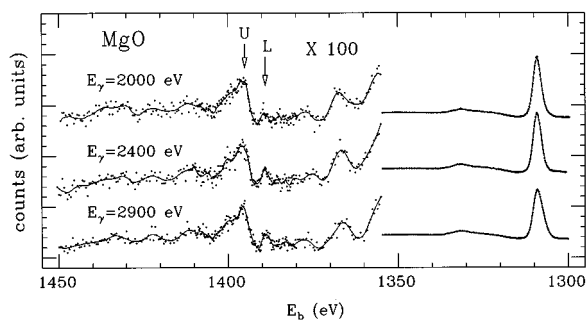


FIG. 3. Photoelectron spectra for MgO at three different photon energies. The vertical scale is normalized to the  $1s$  peak area (visible on the right-hand side). The shake-up region (left-hand side) is magnified 100 times. Arrows indicate lower “L” and upper “U” components.

and peak energies. Present results confirm, in a wider range of photon energies, previous findings with a different experimental setup.<sup>10,11</sup>

A quite interesting issue to be addressed regards the possible detection of an energy dependence of the satellite spectrum. The comparison of spectra collected with Mg and Al  $K\alpha$  sources<sup>10</sup> on NaCl indicated a possible increase of the lower-upper intensity ratio upon increasing the energy. The comparison among the present spectra in Fig. 2 and also with previous results on NaF (Ref. 11) indicates a further reduction of the upper peak intensity with increasing  $E_\gamma$ .

With presently available experimental evidence it is not possible to exclude spurious effects associated with instrumental characteristics or transmission functions and mean free path. Special care should in any case be taken when comparing spectra recorded with different photon sources and analyzer. In addition the simultaneous apparent increase of the background step through the shake-up features, visible in Fig. 2, complicates the evaluation of peak intensity.

According to the current interpretation the shake-up cross section is expected to reach the asymptotic sudden limit value much closer to threshold than in the presently investigated photon energy interval. Any observation of an intensity energy dependence, if confirmed, would be extremely surprising and stimulates further theoretical and experimental investigations.

### B. MgO

MgO XPS spectra were previously collected with laboratory equipment<sup>12</sup> but the high secondary electron background and the intrinsic characteristics of the spectrometer prevented the authors from obtaining accurate line shapes. Present results allow us to perform a more accurate determination of the shake-up spectral features. Previous results<sup>12</sup> are confirmed but the present experiment is characterized by an improved energy resolution.

Photoelectron spectra were collected at several photon energies  $E_\gamma = 2000, 2400,$  and  $2900$  eV, using a 100-eV pass energy. The XPS spectra, shown in Fig. 3, cover a wide range of binding energies ( $E_b = E_\gamma - E_{\text{kin}}$ ) in the region of the  $1s$  satellites. The spectra are normalized to the area of the  $1s$  peak shown in the right-hand side of the figure. Spectra are magnified by a factor of 100 in the higher-binding-energy

side, where  $KL$  shake-up satellites are located. The FWHM was found to be 2.75, 2.8, and 3.35 eV for spectra collected at  $E_\gamma = 2000, 2400,$  and  $2900$  eV, respectively.

Several features can be recognized in the XPS spectra. At about 1365 eV there is the  $2p$  loss peak. It is found to be about 56 eV higher in binding energy than the main  $1s$  peak, a value consistent with the binding energy of the  $2p$  electrons in Mg (around 50 eV). The second evident feature is found in the 1390–1400-eV binding-energy region. It is associated with the  $1s2p$  ( $KL$ ) shake-up doublet. The energy of the doublet (see Table I) is consistent with previously published self-consistent calculations.<sup>3</sup> The splitting is found to be around 6 eV. The other features found at higher binding energies, although of lower intensity and recorded with a coarser energy step, are found to be reproducible as a function of the photon energy. The two small humps found in the region 110–130 eV above the  $1s$  binding energy can be associated with the  $1s2s$  ( $KL_1$ ) shake-up satellites.

The  $KL$  doublet in the MgO case has a very particular shape. The triplet peak ( $L$ ), found at about 80 eV higher in binding energy than the  $1s$ , has a very tiny intensity with respect to the main singlet feature ( $U$ ). This occurrence was already observed at lower photon energies ( $E_\gamma = 1486.6$  eV) where a distinct triplet peak could not be resolved.<sup>12</sup> It is interesting to note that there is clear evidence that the intensity of the triplet peak increases with the photon energy. The broad feature accompanying the singlet peak ( $U$ ), extending for about 10 eV, can be attributed to several effects. This peak around 90–95 eV can be associated with the energy loss edge due to the excitation of  $2s$  electrons in the medium. However, important solid-state effects can occur in this oxide (see discussion in Ref. 3) leading to broadening and complications of the spectral features. Further  $KL$  photoemission studies using tunable photon energy, better resolution, and enhanced signal-to-noise ratio (presently quite difficult to perform) are necessary for a quantitative evaluation of the observed energy trends and of the complex spectral features.

### C. Al<sub>2</sub>O<sub>3</sub>

To our knowledge, no evidence for shake-up peaks in Al compounds existed before the present experiment. A rough energy estimate indicated the interested region to be between 100 and 120 eV on the  $\Delta E_b$  scale. Photoelectron spectra of Al<sub>2</sub>O<sub>3</sub> single crystal were recorded at three different photon energies, namely,  $E_\gamma = 2000, 2500,$  and  $3500$  eV in order to avoid possible contaminations from Auger peaks. The analyzer pass energy was 100 eV in all cases. The results are shown in Fig. 4 on the common  $E_b$  energy scale. Figure 4 includes the  $1s$  peak region and the shake-up satellite region magnified 100 times. The dots represent the actual experimental points while the smooth solid line is only a guide for the eye. In all spectra the  $2p$  shake-up features are clearly identified. The spectra are normalized to the  $1s$  peak area. The  $1s$  peak FWHM increases from 2.6 eV at 2000 eV, to 2.9 eV at 2500 eV, to 3.9 eV at 3500 eV. At this last energy the profile is slightly asymmetric, probably because of charging fluctuation in this particular acquisition. The width of the main shake-up satellite (indicated with a vertical dashed line in Fig. 4) is roughly equal to that of the  $1s$  peak and no major trends in intensity ratio can be detected. The shake-up

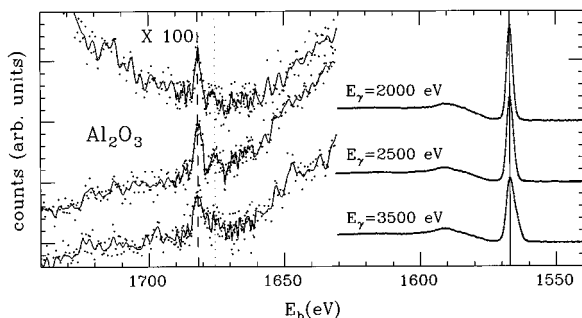


FIG. 4. Photoelectron spectra for  $\text{Al}_2\text{O}_3$  at three different photon energies. The vertical scale is normalized to the  $1s$  peak intensity (visible on the right-hand side). The shake-up region (left-hand side) is magnified 100 times. Lower and upper components are roughly indicated with dotted and dashed vertical lines, respectively.

to  $1s$  intensity ratio is found to be 0.6(1)%. On the right-hand side of the main shake-up peak a weak second component (identified as lower component) is consistently seen in the three spectra. Its intensity is about 0.2(1)% of the  $1s$  peak and the splitting between the two components is about 6.3(2) eV in agreement with the expected  $1s$ - $2p$  exchange interaction effect.

#### D. $\text{SiO}_2$

Also for Si we have obtained direct evidence for the existence of  $2p$  shake-up satellites in XPS spectra. The spectra, reported in Fig. 5 on a binding-energy scale, are both recorded at  $E_\gamma = 3300$  eV and using a 200-eV pass energy. This was required to increase the count rates; the resulting  $1s$  FWHM is about 5.2 eV. The upper spectrum refers to the  $\alpha$ - $\text{SiO}_2$  single crystal, the lower spectrum to a thick  $\text{SiO}_2$  film thermally grown on a Si(100) wafer. The insets show the shake-up region magnified 50 times. The intensity of the feature is in any case found to be very weak, of the order of 0.25% of the  $1s$  intensity, and this explains the difficulty in the detection. The correctness of the identification is supported by the good correlation between the features recorded in the two spectra of different samples and by the consistency of the energy positions with the predicted  $\Delta E_b$  value.

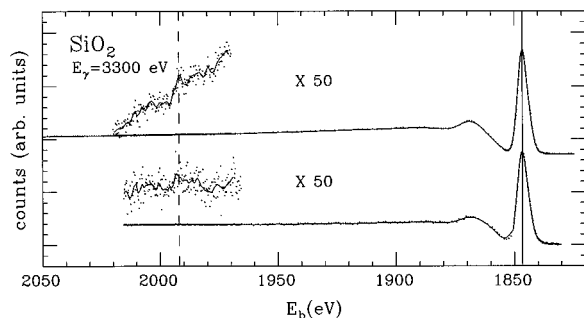


FIG. 5. Photoelectron spectra of crystalline and amorphous  $\text{SiO}_2$  at  $E_\gamma = 3300$  eV. The vertical scale is normalized to the  $1s$  peak intensity. The insets show the shake-up region magnified 50 times. Weak features are systematically visible around  $E_b = 1990$  eV.

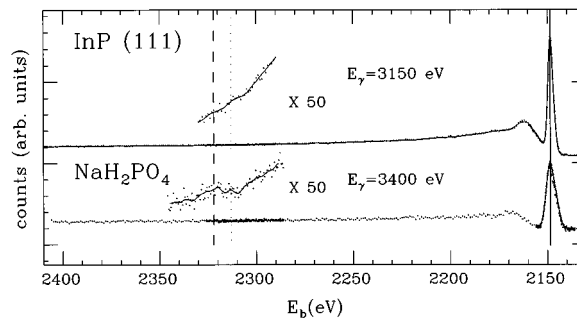


FIG. 6. Photoelectron spectra of cleaved InP (111) and sintered  $\text{NaH}_2\text{PO}_4$  pellet. The vertical scale is normalized to the  $1s$  peak intensity. The insets show the shake-up region magnified 50 times. Shake-up features are visible especially in the  $\text{PO}_4$  compound where P is in a high oxidation state.

The dashed line in Fig. 5 indicates what is tentatively assigned to the upper component. Further experiments are required to provide conclusive evidence and to reveal the satellite pattern.

#### E. InP and $\text{NaH}_2\text{PO}_4$

Experimental evidence of  $2p$  shake-up satellites is also provided for phosphorus compounds. Two samples have been considered in this case. These were a hot-pressed  $\text{NaH}_2\text{PO}_4$  pellet and an InP single crystal cleaved in vacuum along the (111) surface. The spectra collected at slightly different  $E_\gamma$  are reported on the same  $E_b$  scale in Fig. 6.

The extended range InP spectrum has been collected with a 100-eV pass energy, but the extended spectrum of  $\text{NaH}_2\text{PO}_4$  and both expanded spectra for the shake-up regions are collected with a 200-eV pass energy to increase the count rates. The FWHM of the  $1s$  peak is 3.3 eV in InP and 5.8 eV in the  $\text{PO}_4$  salt. The increase is partly due to the increased pass energy and partly to the appearance of a slightly reduced P component associated with decomposed phosphate units. In this case very different compounds have been chosen where the P atom is in a quite different oxidation state. In the  $\text{PO}_4$  compound P is highly oxidized with a formal valence of  $\text{P}^{5+}$  but in InP the P electronegativity is higher and it is formally a  $\text{P}^{3-}$ . The magnified insets of Fig. 6 reveal visible features particularly evident in the  $\text{PO}_4$  compound, as expected. The doubly peaked shape with a splitting of about 8 eV is consistent with the expected pattern and exchange splitting. Also the resulting energy corresponds to the expected value. Very weak features are visible also in InP, the correlation between the corresponding position evidenced by the vertical dashed and dotted lines is striking. However, the weakness of the InP features, of the order of 0.1% of the  $1s$  peak, makes this assignment only a tentative one. The evident difference in shake-up intensity between oxidized and reduced P is consistent with expectation and suggests that systematic studies of shape and intensity can be performed in a wider range of compounds.

#### IV. CONCLUSIONS

The results of the present experiment, summarized in Fig. 1, provide striking evidence for the existence and detectabil-

ity of  $2p$  shake-up satellites on the high-binding-energy side of  $1s$  core-level peaks in photoelectron spectra of third-period elements in condensed phases. The existence of these shake-up channels appears to be a rather general phenomenon in third-period elements. The energy distance of the satellites from the  $1s$  peak ranges from a few tens of eV to a few hundred eV (170 eV for P), well beyond the range where satellite features are commonly observed in XPS. The cross sections are found to decrease with increasing  $Z$ . This is probably due both to matrix element effects and to the actual reduction of available final states for the electron, induced by the progressive filling of the  $3p$  level through the atomic table.

The shape of the shake-up satellites is clearly seen in NaF, MgO, and  $\text{Al}_2\text{O}_3$ . In NaF the observed pattern confirms previous results obtained with laboratory equipment<sup>11</sup> with the clearly split lower and upper components. In MgO a very different pattern is observed. A broad upper feature with a shoulder on the high-binding-energy side is accompanied by a weaker isolated lower feature. Finally, in  $\text{Al}_2\text{O}_3$  the pattern is composed of a strong upper feature and a weaker lower feature. This seems to be reasonably valid also for  $\text{PO}_4$ .

In general it is found that the pattern is always dominated by the lower-upper splitting associated with exchange interaction in the double-hole [ $1s2p$ ] configuration, which is clearly an atomic effect. Solid-state effects appear important in determining the actual lower-upper intensity ratio and are

very effective in lower-symmetry compounds such as MgO.

The main quantitative results for the various elements have been summarized in Table I. The energy position of the satellites is consistent with difference of total-energy calculations. Similarly, the lower-upper splitting is found to increase slightly according to the increase of the  $G^1(1s,2p)$  integral.

The results presented in this paper stimulate further theoretical and experimental investigations. Theoretical questions regard the correct prediction of the satellite pattern intensity and shapes, also for low-symmetry cases such as MgO, and the explanation of the photon energy dependence of the satellite features, possibly revealed, at present, in NaF and MgO. Future experimental efforts may be devoted to broaden the range of elements and compounds and to improve the counting rates. In particular, further investigations and experiments possibly using third-generation synchrotron radiation sources and advanced detectors are encouraged.

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