P $KL_{2,3}L_{2,3}$ resonant Auger spectra in solid phosphorus compounds

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Abstract. P $KL_{2,3}L_{2,3}$ resonant Auger spectra were measured for four insulators (Na_2HPO_4, $Ca_3(PO_4)_2$, Na_2HPO_3 and $CaHPO_3$) and a semiconductor (GaP). Spectator Auger peaks showed both linear energy dispersion and width sharpening around the absorption edges. These peaks are attributed to the Auger resonant Raman effect. Furthermore, it was found that only for the insulators were the Auger peaks split into spectator and normal peaks. This is explained in connection with localized quasi-bound states above the P 1s ionization threshold.

1. Introduction

The recent availability of synchrotron radiation has made it possible to study the details of decay processes with incident x-ray energy ($h\nu$) tuned near the threshold. Interesting new results are being reported for resonant Auger, photoemission and fluorescence processes in both atoms and solids [1]. In particular, investigating the resonant Auger process is quite important from the viewpoint of revealing the mechanisms of photochemical reactions such as photodissociation or photoinduced desorption [2]. There exist two kinds of process [3]. One is a participator Auger process during which an excited electron recombines with a core hole. The other is a spectator Auger process during which the excited electron remains in unoccupied orbitals as a spectator. The former manifests itself as an enhanced intensity of the corresponding photo-line, whereas the latter produces a spectrum similar to the corresponding normal Auger one but has a slightly shifted kinetic energy.

It is well known that the kinetic energy of an Auger electron is peculiar to the element, and is constant even if $h\nu$ is drastically changed and far above the ionization threshold. However, it can change with increasing $h\nu$ near the threshold; this is called the Auger resonant Raman effect. This was first observed by Brown *et al* for the Xe $L_3M_{4,5}M_{4,5}$ process in Xe gas following L_3 deep-core excitation [4]. Later, the same spectra were measured with better resolution by Armen *et al* [5]. They found that the spectator Auger peak shifts to the higher-energy side linearly with $h\nu$ near the threshold. Also in the vacuum ultraviolet region, this was observed for the $M_5N_{2,3}N_{2,3}$ and $N_5O_{2,3}O_{2,3}$ spectra of gaseous Kr and Xe, respectively [6]. For solid systems, several reports exist: e.g. argon-like-ion $L_{2,3}M_{2,3}M_{2,3}$ for ionic solids [7, 8], Ge $M_{2,3}M_{4,5}M_{4,5}$ for Ge [9], Si $KL_{2,3}L_{2,3}$ for SiO_2 [10, 11], P $KL_{2,3}L_{2,3}$ for InP [12] and 4d-metal $L_3M_{4,5}M_{4,5}$ for elemental metals [13].

Recently we measured 4d-metal $L_3M_{4,5}M_{4,5}$ spectator Auger spectra for their compounds [14–16], and S $KL_{2,3}L_{2,3}$ and Cl $KL_{2,3}L_{2,3}$ spectra for molecular adsorbate systems [17, 18]. It was found that the shift energies of the spectator peaks for insulators
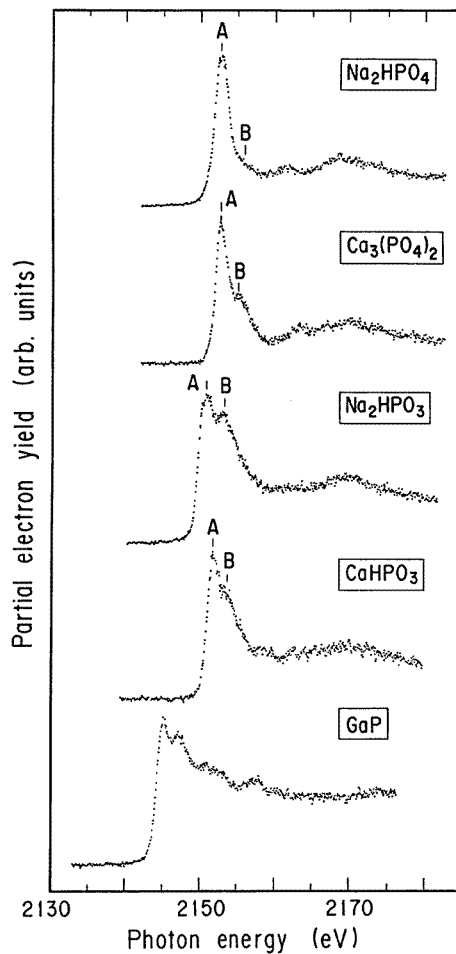
Figure 1. P 1s XANES spectra. See the text for details.

and multilayers were much larger than those for metals and monolayers. This means that the Auger process is strongly related to the electronic structure of solid.

In the present paper we report a further study of the solid-state effect in the resonant Auger process. For this purpose the same P $KL_{2,3}L_{2,3}$ process was compared in compounds which have different electronic structures (four ionic insulators (Na_2HPO_4, $Ca_3(PO_4)_2$, Na_2HPO_3 and $CaHPO_3$) and a semiconductor (GaP)).

2. Experimental procedure

The experiments were carried out using synchrotron radiation at the BL-27A station of the Photon Factory in the National Laboratory for High-Energy Physics (KEK-PF), Tsukuba, Japan.

All of the insulator powders (99.9%) were dried between 200 °C and 350 °C, and pressed into pellets (10 mm diameter and 1 mm thickness). They were heated using an electric blower before being loaded into a preparation chamber to remove carbonaceous

contaminants. The GaP sample was prepared by scraping a GaP(100) wafer in an analysing chamber (base pressure $\sim 1 \times 10^{-8}$ Pa). No decomposition was detected during the experiments, as was verified by the measuring of sharp P 1s, 2p and O 1s photoelectron peaks.

X-ray absorption near-edge structure (XANES) spectra were measured in a partial-electron-yield mode. The detected electron energy was kept $\sim$50 eV below the P KL$_{2,3}$L$_{2,3}$ energy to avoid the charge-up effect. The Auger spectra were measured by a VSW Class 100 hemispherical electron energy analyser.

Data analyses of the Auger spectra were done using a computer program purchased from VSW. Other details are given elsewhere [14–18].

3. Results and discussion

3.1. XANES spectra

Figure 1 shows the P 1s XANES spectra of Na$_2$HPO$_4$, Ca$_3$(PO$_4$)$_2$, Na$_2$HPO$_3$ and CaHPO$_3$, and of GaP. From the dipole selection rule, the main peak structures are considered as P 1s → P 3p* transitions (* means unoccupied orbital). The main absorption peak in each spectrum slightly shifts to the higher-energy side with increasing oxidation number of the P ion.

To the best of the authors' knowledge, P 1s XANES spectra have not been reported for any of the insulators. Here the absorption peaks were qualitatively assigned on the basis of the spectra of P$_4$O$_{10}$, P$_4$O$_6$, PO(C$_6$H$_5$O)$_3$ and P(C$_6$H$_5$O)$_3$ [19] as follows. Na$_2$HPO$_4$ and Ca$_3$(PO$_4$)$_2$ have equivalent basic structures consisting of PO$_4^{3-}$ anions (local symmetry T$_d$). This is the same situation as for P$_4$O$_{10}$ and PO(C$_6$H$_5$O)$_3$ [19] whose P 1s XANES spectra have been measured and interpreted by MS-X$_\alpha$ (MS $\equiv$ multi-scattering) calculations. Therefore, comparing our data with those results, the absorption peaks of Na$_2$HPO$_4$ and Ca$_3$(PO$_4$)$_2$ are roughly assigned. The peaks A and B are the transitions to 6e and 8e + 9a$_1$ + 7e, respectively, and the higher-energy peaks at around 2164 eV and 2170 eV are from shape resonances. On the other hand, both Na$_2$HPO$_3$ and CaHPO$_3$ consist of PO$_3^{3-}$ anions (local symmetry C$_{3v}$). The peak assignments could be made in the above-described manner, referring to the spectra of P$_4$O$_6$ and P(C$_6$H$_5$O)$_3$ [19]. The peaks A and B are considered as the transitions from P 1s to 5e + 5a$_1$ and 6e + 7e, respectively, and the higher-energy structures are from shape resonances.

The spectrum of GaP is quite similar to that in the previous report [20], where the shape of the spectrum was explained by means of theoretical calculations based on both the short-range-order multiple scattering and the effective distributions of charge between Ga and P atoms.

3.2. P KL$_{2,3}$L$_{2,3}$ resonant Auger spectra

Figure 2 shows P KL$_{2,3}$L$_{2,3}$ resonant Auger spectra around the P 1s edge for an ionic insulator: Na$_2$HPO$_4$. Two kinds of peak, marked A and B, are clearly seen. No photoelectron peak and no Auger peak other than that from the P KL$_{2,3}$L$_{2,3}$ process can be located in this energy region, except the C1s peak whose intensity is almost zero. Thus both of them are attributed to the P KL$_{2,3}$L$_{2,3}$ Auger process. Peak A appears when $h\nu$ is tuned at a low-energy rising point of the XANES spectrum ($\sim$2145 eV). One of the remarkable features of the figure is that it shifts like a photoelectron peak to the higher-kinetic-energy side with increasing $h\nu$ up to 2150 eV, which is marked as I_{th}. Its intensity changes
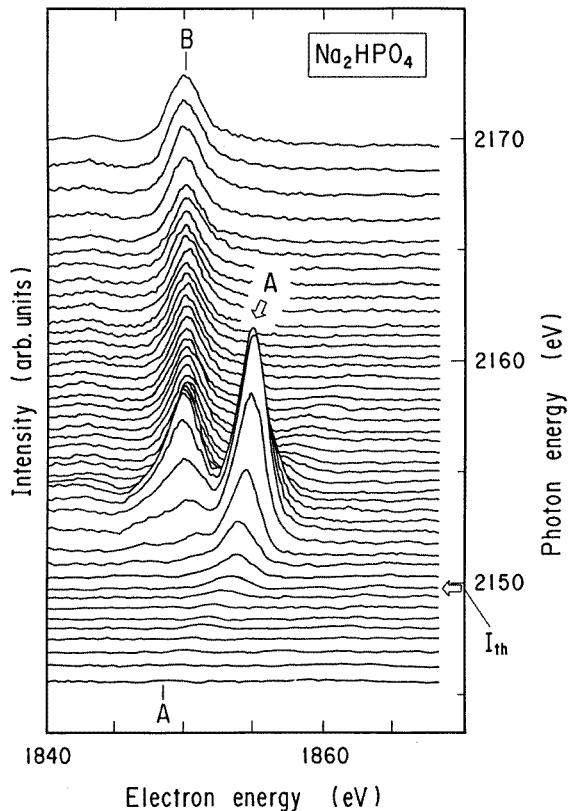
Figure 2. P $KL_{2,3}L_{2,3}$ Auger spectra of Na_2HPO_4 near the P 1s threshold. A and B stand for spectator and normal Auger peaks ($^1D_2$) , respectively. I_{th} means the threshold energy for the normal Auger peak.

according to the XANES spectrum. When $h\nu$ is tuned between 2150 eV (I_{th}) and 2165 eV, another remarkable feature is noticed: that the Auger peak is split into the peaks A and B. The energy shift of the former peak is found also in this $h\nu$-region. Since the energy of the latter peak is almost constant even if $h\nu$ is drastically changed, it is assigned as a normal Auger peak. Therefore the peak A may be considered as a spectator Auger peak. From the resemblance between these spectra and S KLL spectra in sulphur compounds [21], the final-state terms of the main line and the low-energy satellite at $\sim$1843 eV are assigned as $^1D_2$ and $^1S_0$, respectively.

For comparison, the same spectra were measured for the semiconductor GaP. They are displayed in figure 3. Also in this case, there appear two kinds of Auger peak, marked A and B. The former peak shifts with changing $h\nu$ below I_{th}, and the energy of the latter peak is constant in spite of the change of $h\nu$ above I_{th}, as for the spectra of Na_2HPO_4. Thus we judge that the peaks A and B are the spectator and the normal Auger peaks ($^1D_2$), respectively. However, the result is obviously different from that obtained for Na_2HPO_4. That is, the spectator peak continuously merges into the normal one when $h\nu$ is adjusted around I_{th} without the peak splitting.

Figures 4(a) and 5(a) show the intensities of the spectator and the normal peaks plotted against the $h\nu$s. In both they are enhanced around the absorption edges. This means that
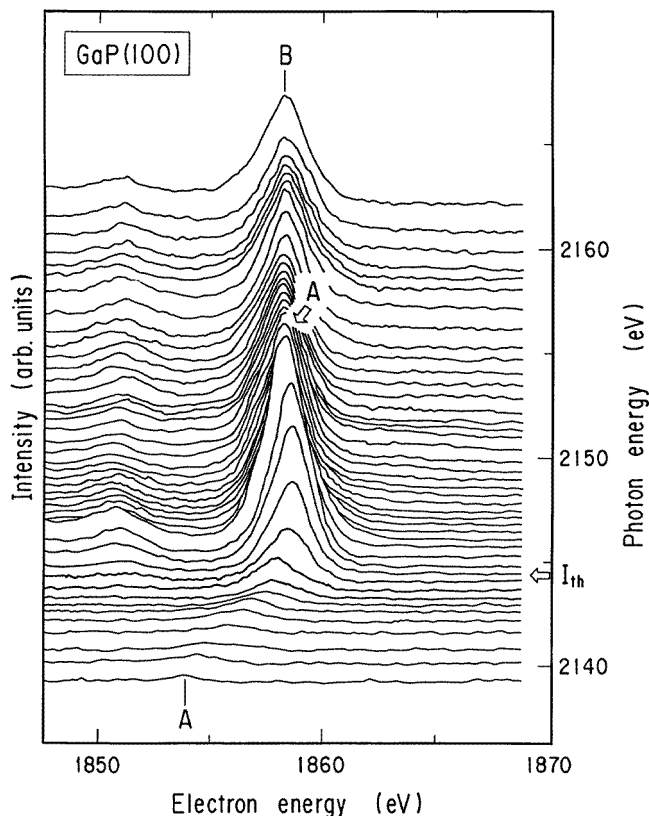
Figure 3. As figure 2, but for GaP.

the peaks arise from phosphorus (i.e., P 1s resonance), not from any other element such as carbon. The most important point in the figures is that the intensities of the spectator and the normal peaks exhibit partial densities of states in the unoccupied orbitals, i.e., the former and the latter correspond to the components of the bound states and the continuum, respectively. Hence it is obvious that the bound states merge deeply into the continuum in Na$_2$HPO$_4$. This implies that quasi-bound states could be formed above the threshold in the insulator. In addition, the sum of the peak intensities follows the XANES spectrum extremely well. This is fairly reasonable because the spectrum were measured by means of the Auger electron-yield method.

The energies of the Auger peaks are plotted against the $h\nu$s in figures 4(b) and 5(b). For the normal peaks, it is seen that they shift very slightly to the lower-energy sides (1.5 eV for Na$_2$HPO$_4$ and 0.3 eV for GaP) with increasing $h\nu$ just above the thresholds. This is the phenomenon well known as the post-collision interaction (PCI) [22], in which core-hole screening is strongly affected by a slowly outgoing photoelectron near the ionization threshold. The most prominent feature in the figures is that the energies of the spectator peaks change almost proportionally to the $h\nu$s, as if they were just photoelectron peaks. Figure 4(a) exhibits another interesting feature: that the dispersion of the spectator peak seems to be divided into the two regions below and above the largest absorption peak at $\sim$2153 eV (marked as 'on-reso.').

For all of the other insulators, the results were generally the same as that for Na$_2$HPO$_4$,
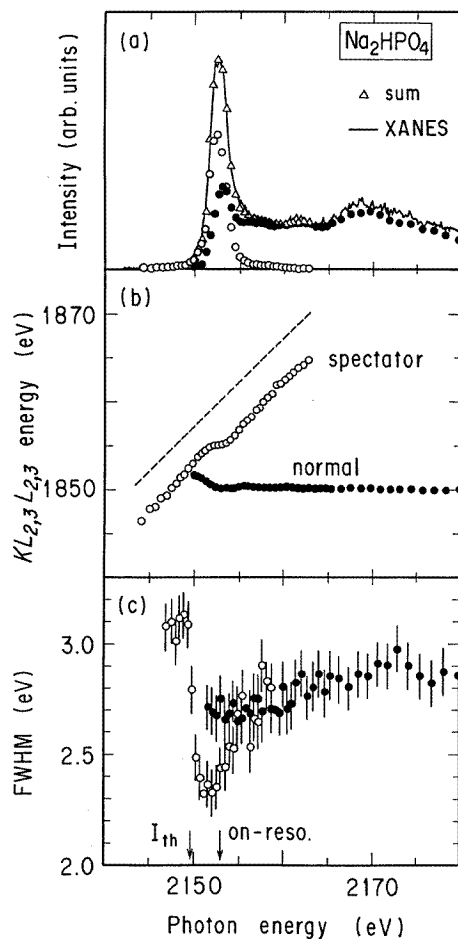
Figure 4. (a) Intensities, (b) energies, and (c) widths (FWHMs) of P $KL_{2,3}L_{2,3}$ ($^1D_2$) Auger peaks plotted against $h\nu$ for Na_2HPO_4. A broken line stands for linear Raman dispersion. The label 'on-reso.' indicates the energy at the largest absorption peak. Error bars stand for statistical errors from the fitting procedure.

Table 1. Shift energies (Δs) and width reduction rates (R_ws) of P $KL_{2,3}L_{2,3}$ ($^1D_2$) spectator Auger peaks, and the existence of Auger peak splitting for all of the compounds.

Material	Δ (eV)	R_w (%)	Peak splitting
Na_2HPO_4	18.5	22.4	Yes
$Ca_3(PO_4)_2$	16.5	23.8	Yes
Na_2HPO_3	15	20.6	Yes
$CaHPO_3$	15	18.3	Yes
GaP	5	14.6	No

i.e., the linear energy shift and the two-step dispersion of the spectator peak, and the Auger peak splitting. The observed shift energies (the Δs) are summarized in table 1 together with that for GaP. It is interesting that the general trend obtained here is quite similar to those
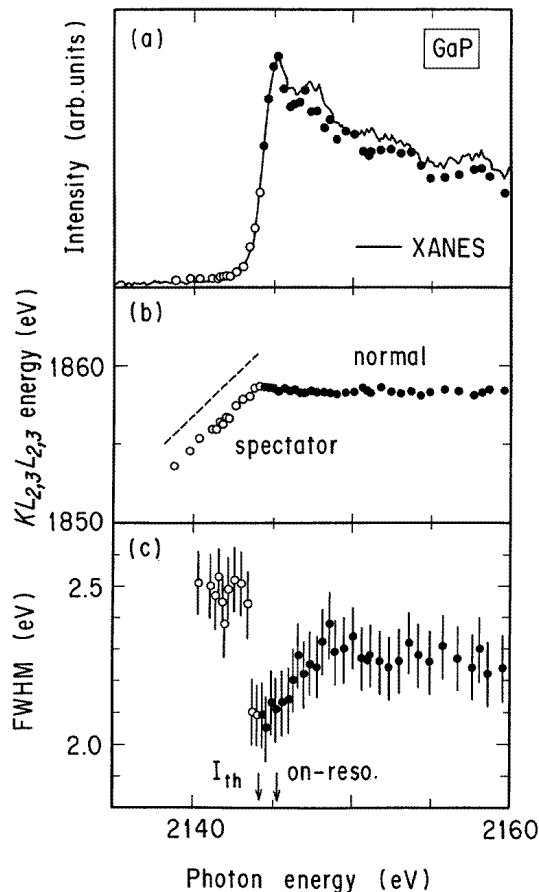
Figure 5. As figure 4, but for GaP.

for 4d-metal L$_3$M$_{4,5}$M$_{4,5}$ spectra for their solid compounds [14–16], and S KL$_{2,3}$L$_{2,3}$ and Cl KL$_{2,3}$L$_{2,3}$ spectra for molecular adsorbate systems (CS$_2$/Cu(100) and SiCl$_4$/Cu(100)) [17, 18]. That is, the results for the insulators are qualitatively the same as those for insulators (Y$_2$O$_3$, MoO$_3$ and so on) and multilayers, whereas for GaP the results are qualitatively the same as those for metallic substances (Nb, Mo and so on) and monolayers. Thus it is considered to be reasonable that we apply the discussions from the above reports to the present results.

The linear energy shift of the spectator peak is the most characteristic feature of the Auger resonant Raman effect [4, 23]. This was named after a similar energy shift of inelastically scattered photons observed in resonant Raman scattering (RRS) [24]. Taking into account the resemblance between the spectator Auger and RRS: that both of them are second-order quantum processes occurring by way of the intermediate excited states, the linear energy dispersion is expected for the former process as well. Briefly speaking, such dispersion may be commonly found if the intermediate states are discrete bound states, because they do not have to conserve the initial-state energy [23–25]. This effect was reported for several systems as mentioned in section 1. However, it is a relatively novel result that different energy dispersions are observed for compounds which contain the same

element but have different electronic structures.

Another characteristic feature of the Auger resonant Raman effect is the line sharpening—in other words, the width of the spectator peak is governed by that of the incident photon rather than the natural width of the inner-shell orbital [6]. This was theoretically predicted [12]; however, it has hardly ever been observed since the width of the incident photon must be narrower than that of the inner shell (in the present case, $\Gamma(P_{1s}) = 0.53$ eV [26]). So only a few cases have been reported such as those for Xe $L_3M_{4,5}M_{4,5}$ [4], Kr $M_5N_{2,3}N_{2,3}$ and Xe $M_5O_{2,3}O_{2,3}$ [6], Pd $L_3M_{4,5}M_{4,5}$ [13], S $KL_{2,3}L_{2,3}$ and Cl $KL_{2,3}L_{2,3}$ [18], and Sr $L_3M_{4,5}M_{4,5}$ [27]. The results obtained in the present work are shown in figures 4(c), 5(c) and table 1. On glancing at figures 4(c) and 5(c), it is seen that the dips are located near the thresholds (the I_{th}s). This is consistent with theoretical consideration [28], calculations [4, 13, 23, 24], and the above-mentioned experimental results. The FWHM (full width at half-maximum) values at these excitations are reduced to 2.4 eV for Na_2HPO_4 and 2.1 eV for GaP, which are ~22% and ~15% less than those of the normal ones, respectively. These values, defined as the width reduction rates (the R_ws), are shown for each system in table 1. For other systems already reported, the value ranges from 40 to 20 [4, 6, 13, 18, 27]. This deviation occurs because the widths of the spectator and normal peaks are governed by those of the incident photon [6] and the inner shells, respectively.

The Auger peak splitting is assumed to be explained in connection with localized bound states even above the threshold [16, 18]. The 1s resonant excitation slightly above the threshold decays through two $KL_{2,3}L_{2,3}$ channels; (1) the excited electron forms localized quasi-bound states until the Auger electron emission occurs, which decay through the spectator process, or (2) the excited electron escapes to the continuum, leading to a $1s^{-1}$ state, which decays through the normal process. The spectra of GaP suggest that only process (2) can occur above the threshold, marked as I_{th} in figure 3. This is probably because the core hole is screened by doped carriers. Thus only the normal Auger peak is observed. On the other hand, it is considered that both of the processes (1) and (2) may happen in the insulators because there exist almost no carriers. Thus the two kinds of $KL_{2,3}L_{2,3}$ peak appear in the same spectrum, and the Auger resonant Raman effect is also observed above the threshold. In the present study the quasi-bound state slightly above the threshold is manifested as the peak B in figure 1 for each compound. This fact seems to explain the two-step energy dispersion of the spectator Auger peak as follows. In all of the insulators, there exist two excited states, manifested as the peaks A and B, near the threshold. They decay through two kinds of $KL_{2,3}L_{2,3}$ spectator Auger process with different final states of the P ion. Hence it is appropriate to assume that the energy dispersions below and above ~2153 eV ('on-reso.') in figure 4(b) correspond to the spectator processes following the excitations to the peaks A and B, respectively. The same situation was found also for Cl $KL_{2,3}L_{2,3}$ in multilayered $SiCl_4/Cu(100)$ [17, 18].

4. Conclusion

P $KL_{2,3}L_{2,3}$ resonant Auger spectra were measured for both insulators (Na_2HPO_4, $Ca_3(PO_4)_2$, Na_2HPO_3 and $CaHPO_3$,) and a semiconductor (GaP). For all of the compounds, the Auger resonant Raman effect was observed, i.e., the linear energy shift and the sharpening of the spectator Auger peak. Furthermore, the Auger peak splitting into the spectator and the normal peaks was found only for the insulators. This is explained in connection with localized quasi-bound states above the threshold.

Acknowledgments

References

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