Do all nuclei recoil on photoemission in compounds?

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Abstract. Hard and soft x-ray photoelectron spectroscopy was performed for core and valence electrons in solid compounds containing V and O atoms. The single-nucleus recoil effects on photoelectron emission were observed in the form of recoil shifts for all core levels and the valence band in a heavy Fermion material LiV\textsubscript{2}O\textsubscript{4}, whereas such shifts were negligible in VO\textsubscript{2} even in the high-temperature metal phase. The valence band recoil shifts of V\textsubscript{5}O\textsubscript{9} and V\textsubscript{2}O\textsubscript{3} metal are found to be in between. These differences in the valence band are ascribable to the difference in the relative spectral weight of the O 2p component near the Fermi level.
Photoelectron spectroscopy (PES) is a direct method of probing the electronic structures of materials [1]. Chemical information can be obtained by core level PES and the extended nature of valence electrons can be obtained by the valence-band PES in compounds [2]–[5]. The usefulness of PES is seen, for example, in the study of high $T_c$ cuprate superconductors [2]. In strongly correlated electron systems, the bulk sensitivity of soft x-ray PES (SXPES) and moreover hard x-ray PES (HAXPES) is recognized to be essential [3]–[6]. Even though the photoionization cross section decreases dramatically with the increase of photon energy $h\nu$ in the x-ray region, the possible extremely high energy resolution of the x-ray optics for HAXPES is very attractive for performing high-resolution PES studies of genuine bulk electronic structures. Meanwhile for atoms and small molecules, the nucleus (or strictly speaking, ion) recoil effects on photoemission are recognized [7]–[9]. Similar recoil effects can be felt on shooting a bullet from a pistol in accordance with the momentum conservation law. HAXPES enabled one to observe the recoil effects in monatomic solids [10, 11]. There was wide general interest in knowing how recoil effects are induced in solid compounds in analogy to the Mössbauer effect [12] and whether the HAXPES spectra are noticeably influenced by the recoil effects. We have performed here SXPES and HAXPES for a heavy Fermion material LiV$_2$O$_4$ [13]–[15] and metal-to-insulator transition (MIT) systems VO$_2$ [16, 17], V$_5$O$_9$ [18] and V$_2$O$_3$ [19] in the metal phase, which contain the common V–O$_6$ octahedron, besides a very light element Li in LiV$_2$O$_4$. It is found that even the spectral shapes of the valence band are modified by the recoil effects in some materials, where the high energy resolution cannot be achieved even if both x-ray and electron optics satisfy the requirement for high energy resolution.

2. Experimental

The samples employed in the present experiments are LiV$_2$O$_4$, VO$_2$, V$_5$O$_9$ and V$_2$O$_3$. Spinel-type LiV$_2$O$_4$ has geometrical spin frustration and shows heavy Fermion behavior below $\sim$ 20 K. Single crystals were grown by a flux method. VO$_2$ shows the MIT from a metallic rutile structure to an insulating monoclinic structure on decreasing the temperature through 340 K. The MIT temperatures of V$_5$O$_9$ and V$_2$O$_3$ are $\sim$ 135 and $\sim$ 155 K, respectively. Whole samples were fractured in an ultrahigh vacuum of better than $\sim$ 5 x $10^{-8}$ Pa to provide clean surfaces. HAXPES was performed at BL19LXU of SPring-8 [20]. The horizontally polarized light was incident onto the sample surface near an incidence angle $\theta$ of 60° from the surface normal direction. Most measurements were done in the nearly normal emission configuration.
Sometimes larger $\theta$ values (up to 80°) were employed to realize the higher counting rate by reducing the light penetration depth from the sample surface. Then the off-normal emission by up to 20° was measured. An MBS A1-HE hemispherical analyzer was employed for the measurements. The long-term stability of the high voltage power supply for this analyzer at 8 kV was measured and found to be within ±8 mV over several hours. Calibration of the binding energy ($E_B$) was made by the Au Fermi edge. The slope error of the employed electronics is less than $5 \times 10^{-5}$. In the case of core level measurement at an $E_B$ of 530 eV, for example, the maximum error induced by this effect is $< 27$ meV. The effect of slope error is much smaller for smaller $E_B$. The total energy resolution of the apparatus was checked near $h\nu = 8$ keV to be better than 70 meV, whereas the resolution was set to about 130–250 meV (FWHM) to have enough counts for the V 3d valence state with very low photoionization cross section [21]. SXPES was performed at BL25SU of SPring-8 [22]. The circularly polarized light was incident on the sample at a $\theta$ of about 45°. The $E_B$ calibration was likewise made by the Au Fermi edge.

The preparation of the surfaces was done in a manner similar to HAXPES. All measurements were made in the near-normal emission configuration.

Owing to the above-mentioned calibration method, the $E_B$ values of shallow core levels of heavy nuclei are found to lie within 20–30 meV between HAXPES and SXPES as seen, for example, in the case of the Yb 4d core level compared with the B 1s core level in Yb$_{2/8}$Lu$_{1/8}$B$_{12}$ [23, 24]. The reproducibility of the $E_B$ of core levels is better than 20–30 meV in both HAXPES and SXPES.

3. Results and discussion

The Li 1s and O 2s spectra of LiV$_2$O$_4$ measured at 20 K and at two different excitation photon energies $h\nu$ are compared in figures 1(a) and (c). For a direct comparison of the spectral shapes, one of the spectra is broadened to have the same resolution as the other one. Then the HAXPES spectrum is shifted to lower energies to have the largest overlap of the part with smaller $E_B$ than the peak $E_B$. One notices that the Li 1s HAXPES spectrum at $h\nu = 8180$ eV is much displaced toward higher $E_B$ in comparison with the SXPES spectrum at $h\nu = 1249.5$ eV. This shift is evaluated as $\sim 530$ meV for the Li 1s core level (figure 1(b)). The shift is likewise evaluated as $\sim 230$ meV for the O 2s core (or inner valence) level (figures 1(c) and (d)). The O 1s spectral shapes in figure 2(a) have shown a noticeable difference between SXPES and HAXPES. Namely, the HAXPES spectrum is much narrower than the SXPES spectrum and the low $E_B$ threshold part of the main peak is displaced by about $\sim 230$ meV (figure 2(b)). This shift is much larger than the possible slope error from a high voltage power supply. The shoulder near $E_B = 531$ eV in the HAXPES spectrum (figure 2(a)) is a bulk intrinsic feature as judged from the high kinetic energy above 7.6 keV [25]. These shifts of the core and inner valence level peaks and their low $E_B$ thresholds cannot be explained without considering the recoil effects. The recoil shift of the order of $\sim 80$ meV is also observed for the V 2p spectra (not shown here).

Now the valence-band spectra are displayed in figure 2(c). One notices two spectral features, one near the Fermi level ($E_F$) and the other in the region between $E_B = 0.5$ and 2.0 eV in SXPES, which are interpreted as the coherent and incoherent peaks [4]. The former feature crosses $E_F$ with relatively high intensity, being consistent with the heavy Fermion behavior [26]. It is clearly seen that the more bulk-sensitive HAXPES spectrum crosses $E_F$ with
Figure 1. SXPES and HAXPES spectra of the Li 1s and O 2s states of LiV$_2$O$_4$ at 20 K. (a) Li 1s core-level spectra measured at $h\nu = 1249.5$ and 8180 eV with instrumental energy resolutions of 215 and 207 meV, respectively. (b) Li 1s spectra. Both spectra are shown with the same resolution of 215 meV and HAXPES is shifted by 530 meV. (c) O 2s spectra measured at $h\nu = 1249.5$ and 7948.8 eV at 20 K with resolution of 215 and 201 meV. (d) O 2s spectra. HAXPES is broadened to 215 meV and shifted by 230 meV.

Recoil effects are well known in the process of $\gamma$-ray emission between two nuclear levels, where a small part of $h\nu$ is converted into the kinetic energy of the recoiling nucleus because of momentum conservation. However, Mössbauer found a recoilless nuclear resonance absorption known as the Mössbauer effect [12], where the momentum is transferred to the total translational...
Figure 2. SXPES and HAXPES spectra of LiV$_2$O$_4$ at 20 K. (a) O 1s spectra measured at $h\nu = 1249.5$ and 8180 eV with resolutions as in figure 1(a). (b) O 1s spectra. The HAXPES is broadened to 215 meV and shifted by 230 meV. (c) Valence-band spectra measured at $h\nu = 1249.5$ and 7948.8 eV with the resolution as in figure 1(c). (d) Valence-band HAXPES is broadened to 215 meV and shifted by 120 meV toward $E_F$. (e) Valence-band SXPES was measured at 708 eV with a resolution of 82 meV (not shown). Then it was shifted by $E_R = 78$ and 250 meV, tentatively simulating the single-nucleus recoil shifts for V and O. They were then broadened by the resolution of 201 meV. The observed HAXPES was compared with the weighted sum of these two components as displayed by the thick solid curve named ‘V 3d’+‘O 2p’, where we found that the low $E_B$ threshold is well reproduced by the sum of the V 3d component with a relative weight of 0.66 (78 meV shifted component shown by the thin dashed curve) and the O 2p component with a relative weight of 0.34 (250 meV shifted component shown by the thin solid curve).
Figure 3. SXPES and HAXPES spectra of metallic VO\(_2\), V\(_2\)O\(_3\) and V\(_5\)O\(_9\). (a) O 1s spectra of VO\(_2\) at 350 K measured at \(h\nu = 1250\) and 7932 eV with energy resolutions of 400 and 250 meV, respectively. (b) Valence-band spectra of VO\(_2\) at 350 K measured at \(h\nu = 700\) and 7932 eV with the resolutions of 150 and 250 meV. (c) Valence-band spectra of metallic V\(_2\)O\(_3\) (V\(_5\)O\(_9\)) measured at \(h\nu = 700\) and 7932 eV and at 175 K (150 K) with a resolution of 130 (250) meV in comparison with those of LiV\(_2\)O\(_4\).

motion of the whole crystal, resulting in no recoil effects. The probability of the recoilless process is given by

\[ f = \exp((-1.5(h^2v^2/2Mc^2)/k_B\theta_D)(1 + 2/3(\pi T/\theta_D)^2)), \]

(1)

at a temperature \(T\) well below the Debye temperature \(\theta_D\), where \(M\) is the nucleus mass and \(k_B\) is the Boltzmann constant. This recoilless probability, which can be noticeable at low \(T\) when \(k_B\theta_D\) is larger than the recoil energy \((h^2v^2/2Mc^2)\), becomes drastically reduced with increasing \(T\), showing clear recoil effects.

If single-nucleus recoil is considered on the photoelectron emission, the recoil energy \(E_R\) is predicted from a simple momentum conservation rule as

\[ E_R = E_K \times m/M, \]

(2)

where \(E_K\) and \(m\) are the electron kinetic energy and mass. In the case of small molecules, the single-nucleus recoil takes place for a certain atom and the resulting \(E_R\) is later shared by three
Table 1. Predicted single-nucleus recoil energy $E_R$ for LiV$_2$O$_4$.

| Element (M) | Core ($E_B$) | $h\nu$ 8000 eV | 1250 eV | 700 eV |
|-------------|--------------|----------------|---------|--------|
| Li (6.941)  | 1s (∼54 eV)  | 627 meV        | 95 meV  | 51 meV |
|             | 2s (∼0 eV)   | 636 meV        | 99 meV  | 55 meV |
| V (50.94)   | 3d (∼0 eV)   | 86 meV         | 13 meV  | 7 meV  |
| O (16.00)   | 1s (530 eV)  | 256 meV        | 25 meV  | 6 meV  |
|             | 2s (22 eV)   | 273 meV        | 42 meV  | 23 meV |
|             | 2p (∼0 eV)   | 274 meV        | 43 meV  | 24 meV |

terms, namely, center-of-mass translational motion and vibrational and rotational excitations. In solids, however, the last term is unimportant and the first term is thought to be negligible because the corresponding mass is very large. Then the second term, namely phonon excitation, becomes most important. Even in the case of heteroatomic solids, the recoil shift is predicted to be equal to the above-mentioned $E_R$ in the single site harmonic phonon approximation [27]. Still it should be recalled that phonon excitation is a result of nucleus recoil. If electron–phonon interaction takes place first, the recoil shift will be represented by the characteristic phonon energy irrespective of different core and valence electron excitation and may appear in all materials, which is not the present case. According to equation (2), the single-nucleus recoil shift $E_R$ between 8 keV and 1250 eV is estimated as 532 meV for the Li 1s state and as 231 meV for both O 1s and O 2s states in LiV$_2$O$_4$, as summarized in table 1. The experimentally observed recoil shifts of ∼530 meV for the Li 1s core and ∼230 meV for both O 1s and 2s states are fully consistent with this prediction for single-nucleus recoil. Once such a recoil takes place for any nucleus on the occasion of photoelectron emission, it may also be observable for other core states of this nucleus with $E_R$ predicted by equation (2). Then the predicted $E_R$ between 8 keV and 1250 eV is 70, 540 and 230 meV for the V 3d, Li 2s and O 2p states, respectively.

The recoil shift of the V 3d-dominated valence band in LiV$_2$O$_4$ up to ∼120 meV between ∼8 keV and ∼1250 eV deviates significantly from the predicted $E_R$ shift of 70 meV for the V 3d state. It also deviates a lot from the predicted $E_R$ of 540 meV for the Li 2s state and 230 meV for the O 2p state. First of all, let us consider the reason why the photoemission of valence electrons extending over the whole crystal can still induce recoil effects irrespective of its huge mass. There is no doubt about the drastic spatial oscillation of the photoelectron plane-wave functions for $E_K$ of several keV. On the other hand, the valence electron wave function oscillates very smoothly in the region away from the nuclei. However, its spatial oscillation becomes suddenly rapid on approaching the nucleus due to the core electron potential [28]. Therefore the photoexcitation matrix element between these final and initial state wave functions is negligible by phase cancellation away from the nucleus but becomes remarkable in the vicinity of the individual nucleus, inducing noticeable single-nucleus recoil effects. Since the valence electron wave function can be expressed by a linear combination of Wannier functions and the quasiparticle is composed of not only the V 3d but also the O 2p and Li 2s states, the magnitude of the observed recoil shift of the valence band could contain additional contributions of the O 2p and Li 2s components besides the V 3d component, as understood from the band calculation [29].

8 The spectral weight of the Li 2s state is less than a few per cent and negligible in the present discussion.
As shown in figure 2(e), the observed recoil shift of the valence band in LiV$_2$O$_4$ is well reproduced by considering the sum of the V 3d and O 2p components with relative spectral weights of 0.66–0.34 near $E_F$, which are shifted by the respective amount of $E_R$.

The O atoms are contained in both the Li–O$_4$ tetrahedron and the V–O$_6$ octahedron in LiV$_2$O$_4$. From the recoil shifts of the low $E_B$ threshold of the O 2s and 1s HAXPES, we see that all O atoms follow the single-nucleus recoil effects in LiV$_2$O$_4$. Namely, the single O and V nuclei can freely recoil in the V–O$_6$ octahedron and so do the Li and O nuclei in the Li–O$_4$ tetrahedron in LiV$_2$O$_4$ at the moment of photoemission. In the case of metallic VO$_2$, however, we found no single-nucleus recoil effects for the V and O atoms, in contrast to LiV$_2$O$_4$. Figure 3(c) shows the recoil shifts in the valence band of V$_2$O$_3$ and V$_5$O$_9$ compared with the result of LiV$_2$O$_4$. Their shifts between $h\nu \sim 700$ and $\sim 8$ keV are $\sim 40$ meV for V$_2$O$_3$ and $\sim 15$ meV for V$_5$O$_9$. Since the single-nucleus recoil shifts predicted by equation (2) are not observed for the V 2p core level but are observed for the O core levels in these materials (not shown here), these results are understood as due to the relative O 2p spectral weight of $\sim 0.2$ (0.1) to the valence band of V$_2$O$_3$ (V$_5$O$_9$) near $E_F$.

We have thus found three representative cases of recoil effects for core levels and valence bands in solid compounds. The criterion for the presence or absence of recoil effects in solid compounds, including nucleus dependence, is a rather complicated problem. One notices, however, that the minimum V–O distance in LiV$_2$O$_4$ (1.97 Å at 20 K) is noticeably longer than that in VO$_2$ (1.92 Å at 350 K). The V–V and O–O distances in these two materials have similar tendencies. One also notices that the shortest V–O distance in the V–O$_6$ octahedron in V$_2$O$_3$ is 1.967 Å [19], which is very close to the value in LiV$_2$O$_4$, whereas most of the V–O distances in V$_5$O$_9$ [18] are close to or even shorter than that in VO$_2$. These differences in V–O distances are in qualitative agreement with the behavior of recoil shifts of the valence-band $E_F$ threshold in these materials.

4. Conclusions

We have observed three typical behaviors of single-nucleus recoil effects for core and valence photoelectron emission in solid compounds with light elements. Nowadays HAXPES is in great demand for probing genuine bulk electronic structures of strongly correlated electron systems. According to the present contrastive results, however, one must pay a great deal of attention to the recoil energy shift of valence-band structures for discussing materials properties. Bulk-sensitive fermiology by hard x-ray angle-resolved PES may be hindered if the recoil effects are substantial. Even if extremely high energy resolution of the experimental set-up is realized in the future, the final experimental energy resolution in HAXPES may be limited by the possible recoil effects in some materials. On the other hand, the presence or absence of valence-band photoelectron recoil effects could provide key information on the character of the quasi-particles in solids.

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