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Calculation of emission spectra of lithium compounds

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Abstract

We studied the electronic structure of lithium metal, lithium fluoride, and spodumene using density functional theory. We performed calculations of the total, local and partial density of states, and x-ray emission spectra. We observed changes in the Li K spectra shape and energy position due to the chemical structure and composition modification. We also outline possible interferences between emission bands.

KEYWORDS

density functional theory, density of states, lithium fluoride, spodumene, x-ray emission spectroscopy

1 | INTRODUCTION

The use of lithium revolutionized the field of batteries and energy storage, leading to a strong and increasing demand for lithium. A deeper understanding of lithium mobility,¹ concentration, and extraction potential, as well as the accurate and easy quantification of Li in various minerals and compounds, are therefore crucial for improving performance. Yet, the detection and quantification of lithium using Li K emission in complex compounds are still not achieved experimentally, due to among other factors its low fluorescence yield, the poor transmission of

spectrometer's windows at very low x-ray energies, and reabsorption resulting in a low-intensity x-ray emission.

To measure emitted X-rays experimentally, X-ray emission spectroscopy (XES) is used. This powerful technique allows the analysis of structural and electronic properties of materials, by measuring the emissions due to valence band-core level or core-core recombination following the ejection of an electron from a core level. In the case of a valence-core transition, leading to a so-called emission band, the occupied valence states are probed, making it element-specific and sensitive to the local chemical environment,^{2,3} in addition to being compatible with *operando* measurements. While there exist numerous articles in the literature regarding the Li K spectrum of metallic lithium, spanning from 1938 to 2021,^{4,5} there is a lack of data for other compounds and alloys.

[Correction added on 13 January 2023, after first online publication:
The name of the second author has been corrected in this version.]

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In particular, we did not find any paper reporting Li K spectrum for minerals, although some of them constitute actually mined lithium ores, as for example spodumene ($\text{LiAlSi}_2\text{O}_6$) contains 8 wt% lithium. For lithium fluoride, LiF, we have found only eight references [6–13], presenting large differences in shapes, width, and energy depending on: the excitation means, electrons or photons; the excitation conditions, electron energy, electron current, and duration of the excitation, ... In these conditions, it would be valuable for the x-ray spectroscopist to consolidate his results by comparing his Li K spectra to those obtained from ab initio calculations. This is all the more important since the recent development of new spectrometers^{14–16} and periodic multilayers¹⁷ to be set up on scanning electron microscopes and electron probe microanalyzers to probe the ultra-soft x-ray range and particularly the Li K emission band around 50 eV.

This work aims to facilitate and contribute to improving the detection of soft x-rays in complex materials using density functional theory (DFT) calculations. With the fast development of computational-based ab initio methods, DFT gained huge popularity in calculating the electronic structure of materials, due to its low computational cost which allows large systems to be studied and obtain core-electron spectroscopy description. An example of these studies is the one carried out by Mukai et al. on Li_2O and Li_2O_2 ,¹⁸ where Li K emission spectra were calculated using DFT and compared to XES experiments. In another example, He et al. performed DFT calculations to obtain the band structure and density of states (DOS) of spodumene, where different exchange-correlation functions were compared to optimize the crystal model.¹⁹

2 | METHOD

DFT calculations were performed using the all-electron linearized augmented plane wave method, in conjunction with Perdew–Burke–Ernzerhof (PBE) functional in ab initio simulation package (WIEN2k).²⁰ This package allows obtaining the total DOS as well as the local ones, referring to the DOS around a given element, and the partial ones, to the DOS of a given symmetry. From the local and partial DOS corresponding to the valence states involved in the transition, the emission spectra were obtained using the electric dipole approximation included within the package. The graphs are referenced to the Fermi energy of each compound. Negative values correspond to occupied states and positive values to empty states. To convert into photon energy scale, core level binding energy data were used from X-ray photoemission spectroscopy (XPS) experiments.^{21–23}

We performed a systematic analysis of the soft X-ray spectra of Li K in different compounds including Li

metal, LiF, and spodumene. Given the dipole selection rule, K spectra depend on the DOS of p symmetry while L spectra on the DOS of s and d symmetry. Consequently, the Li K emission is due to the $2p$ valence states transition to $1s$ core states in lithium atoms and therefore the spectrum reflects the distribution of the p states within the valence band.

The lattice parameters used in the case of Li metal with $Fm\bar{3}m$ point group with the following values $a = b = c = 0.3055 \text{ nm}$ with $\alpha = 60^\circ$, $\beta = 60^\circ$, and $\gamma = 60^\circ$. For LiF, the cell parameters are $a = b = c = 0.4028 \text{ nm}$, with $\alpha = \beta = \gamma = 90^\circ$ with a spatial structure of $Fm\bar{3}m$. Finally for spodumene with the chemical formula $\text{LiAlSi}_2\text{O}_6$, parameters are $a = 0.86274 \text{ nm}$, $b = 0.49871 \text{ nm}$, and $c = 0.75718 \text{ nm}$ with angles $\alpha = 89.737^\circ$, $\beta = 114.072^\circ$, and $\gamma = 90.169^\circ$ with the symmetrical spatial structure $C12/c1$.²⁴

From the calculated DOS, the Li K emission band ($2p-1s$ transition) is obtained by using the local and partially occupied Li p valence states. The obtained spectra are then broadened with the following parameters to take into account the experimental and lifetime broadenings for both core and valence states: the Lorentzian broadening (0.03 eV) coming from the Li $1s$ core hole lifetime²⁵; the Lorentzian broadening (0 to 1.5 eV along the valence band) of the valence states; the Gaussian instrumental broadening (0.5 eV). The 0.5 eV Gaussian broadening is typical of the width of the diffraction pattern of a grating used to disperse X-ray radiation. If a spectrometer equipped with a periodic multilayer would be used, then a Gaussian broadening of 2.5–3 eV would be expected.¹⁷

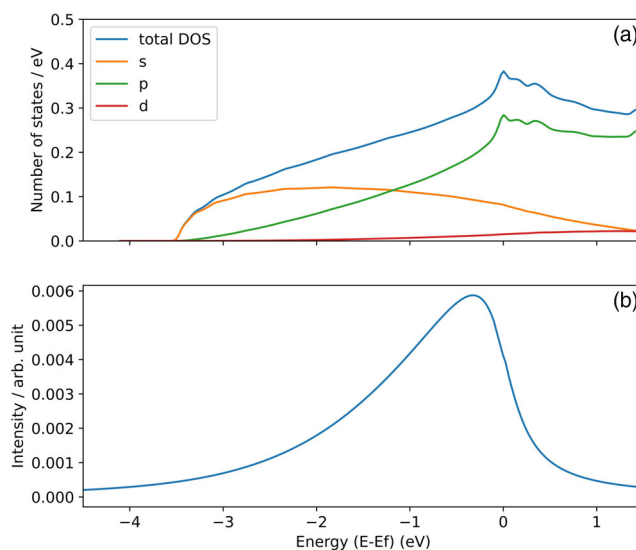


FIGURE 1 Calculated Li local, and partial DOS (a), and Li K emission band of lithium metal (b). [Colour figure can be viewed at wileyonlinelibrary.com]

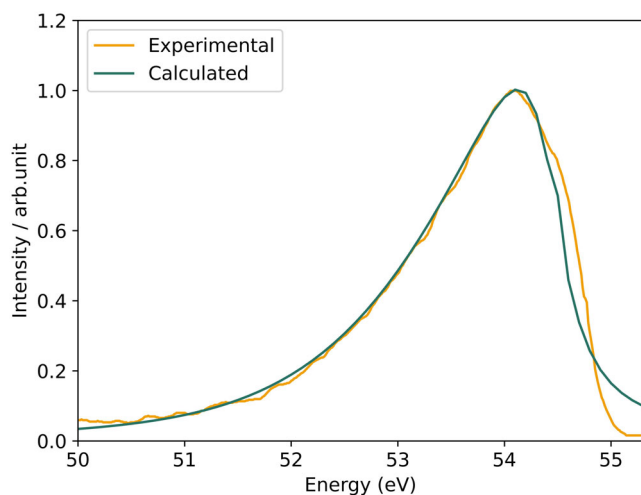


FIGURE 2 Comparison of experimental¹⁸ and calculated Li K emission band in lithium metal. [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/xrs.3329)]

3 | RESULTS AND DISCUSSION

3.1 | Lithium metal

In Figure 1a, the calculated total and partial DOS of lithium metal are presented and compared with the Li K emission spectrum in Figure 1b. The shape of the occupied total DOS is close to the one expected for a good metal. Solid orange, green and red curves represent the contribution of *s*, *p*, and *d* states, respectively. The lower part of the valence band, -3.5 to -1 eV, is dominated by the *s* valence states, while the upper part, -1 eV to E_f , is mostly dominated by the *p* states. The contribution of *d* states is negligible. In Figure 1b, the calculated emission band presents a Doniach–Šunjić line shape reflecting the Li *p* states distribution.

In order to verify the precision of our calculation, a comparison with experimental XES emission from the literature¹⁸ is presented in Figure 2. To put both calculated and experimental spectra on the same photon energy scale, the calculated spectrum should be shifted by a value equal to the binding energy of the Li 1s core level as determined by XPS, 54.78 eV.²¹ But in this case, to align the maxima of both spectra it was necessary to shift the calculation by 56.6 eV. We ascribe this discrepancy to poor calibration of the experimental photon energy scale. Indeed, the energy of the maximum of the Li K emission band is given at 54.3 eV in the Bearden database²⁶ and 54.25 eV in the Cauchois and S  nemaud data table.²⁷ The obtained figure reveals a clear superposition of the two spectra, except in the region of the Fermi level where self-absorption occurs.

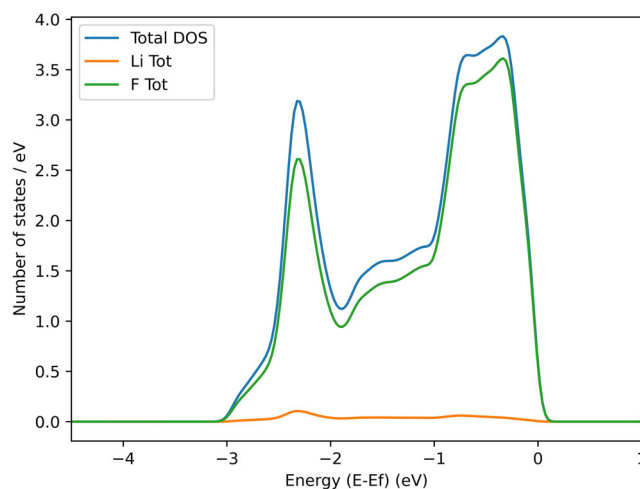


FIGURE 3 Calculated total and local DOS of Li and F in LiF. [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/xrs.3329)]

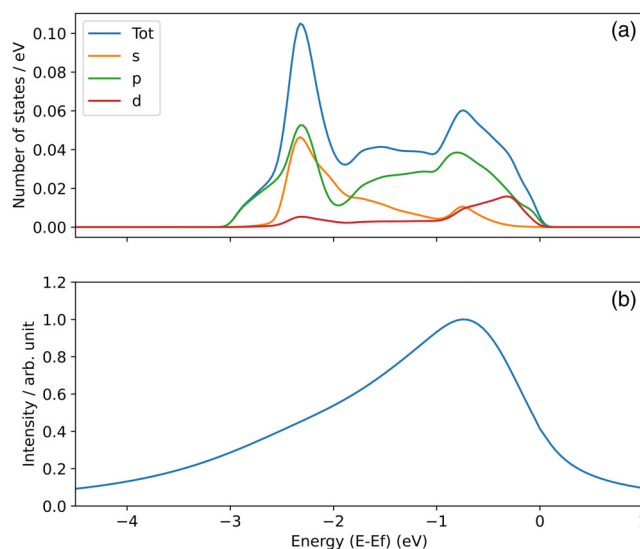


FIGURE 4 (a) Calculated Li local and partial DOS, and (b) Li K emission spectrum in LiF. [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/xrs.3329)]

3.2 | Lithium fluoride

Figure 3 represents the total DOS (blue) and local DOS of Li (orange) and F (green) in LiF. The total DOS is formed of a large band ranging from -3 to 0 eV, containing two peaks, the first at -2.3 eV and the second centered around -0.5 eV. The occupied valence band is dominated by the DOS of fluorine emerging mostly from its *p* states (not shown). The absence of the unoccupied states (positive energies) is due to the insulating properties of LiF presenting a forbidden bandgap of 14 eV.²⁸

Figure 4a represents the local and partial DOS of Li in LiF. They present a wide band between -3 and 0 eV

FIGURE 5 Total and local DOS of spodumene [Colour figure can be viewed at wileyonlinelibrary.com]

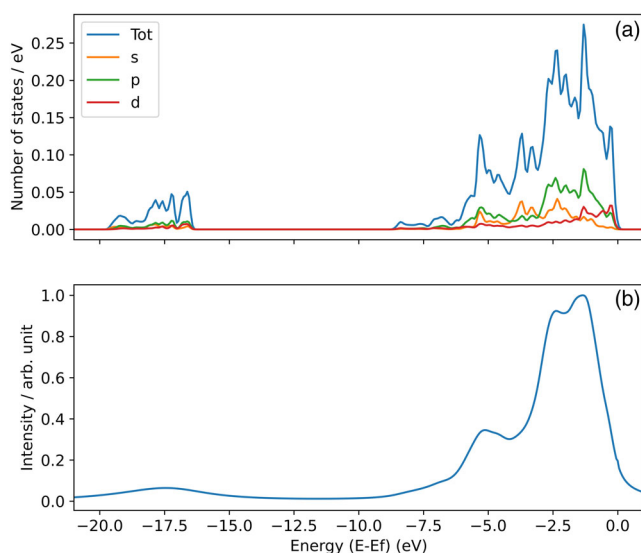
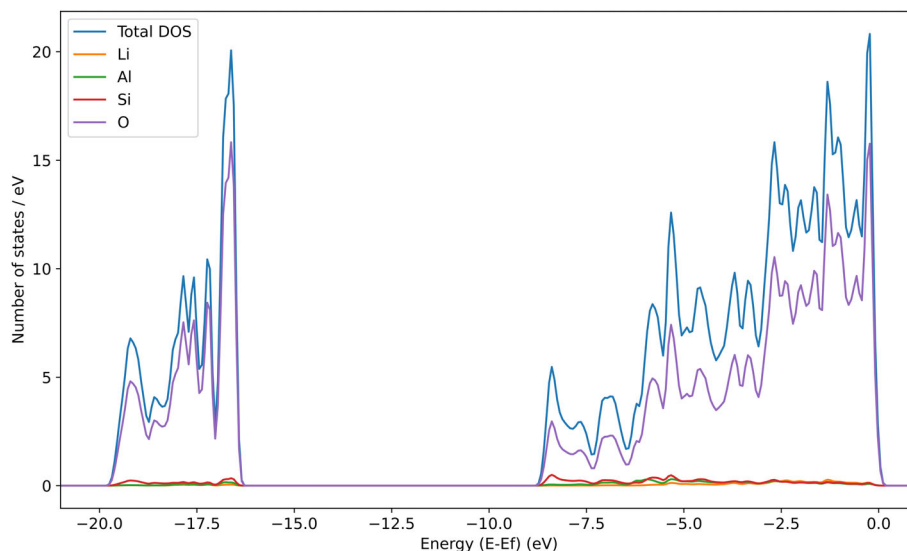


FIGURE 6 Calculated (a) local and partial Li DOS and, (b) Li K emission spectrum of Li in spodumene. [Colour figure can be viewed at wileyonlinelibrary.com]

with two peaks located at -2.3 eV and -0.8 eV. The peak at -2.3 eV is dominated by both *s* and *p* states, while the top of the valence band is dominated by *p* states with a non-negligible contribution of *d* states at the highest energies. This bandwidth and peak positions correspond to the fluorine *p* partial DOS, resulting in the formation of a highly mixed DOS in the interval -3 to 0 eV, and therefore, forming the Li K emission spectrum presented in Figure 4b. In the calculated Li K emission band, we observe one main asymmetric peak, with a full width at half maximum (FWHM) of 1.58 eV. Owing to the introduced broadenings, it is not possible to see all the features of the Li *p* DOS in the Li K spectrum.

3.3 | Spodumene

The calculated total and local DOS of spodumene are presented in Figure 5. In the total DOS, we can distinguish two valence regions, a lower one called the lower valence band (LVB) from -20 to -16 eV and the upper one called the upper valence band (UVB). For oxygen, there are three inequivalent atoms in the unit cell. The sum of the three corresponding local DOS is shown in Figure 5. The LVB is dominated by the oxygen *s* states, while the UVB is dominated by the oxygen *p* states (not shown). The Li, Al and Si local DOS are only a fraction of the oxygen local DOS. The valence and conduction band are not intersecting at the Fermi level owing to a calculated bandgap of 5.4 eV making spodumene an insulator.

The Li local DOS and *s* (orange), *p* (green), and *d* (red) partial DOS of lithium in spodumene are shown in Figure 6a. The LVB and UVB are easily differentiated. The hybridization of oxygen and lithium valence states makes reproducing most of the features of the oxygen local DOS in the lithium local DOS. The calculated Li K spectrum of spodumene, Figure 6b, has an asymmetric peak with its maximum at -1.6 eV and FWHM of 2.6 eV. A lower energy shoulder extends at -5 eV, associated with low-lying *p* valence states in the range -4.5 to -6 eV, Figure 6a. In addition, secondary peak is present in the low energy range at -17.5 eV associated with transitions from *p* valence states of the LVB.

3.4 | Comparison of Li K emission bands

The Li K emitted photons carry information about the occupied DOS and the chemical environment of the lithium atoms. Any variation of those will lead to a change

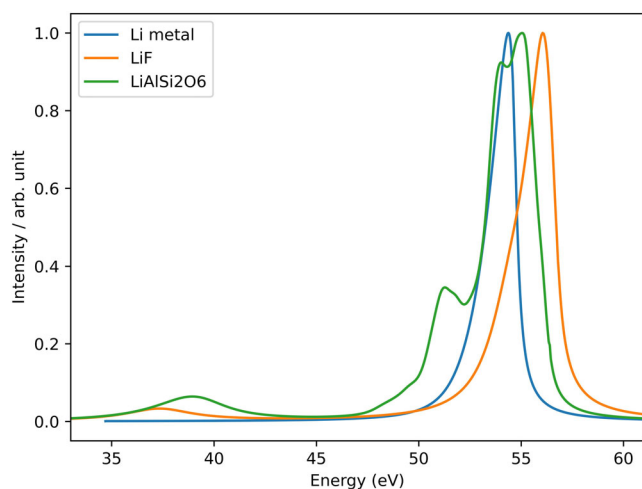


FIGURE 7 Comparison on a photon energy scale of the calculated Li K emission in lithium metal, lithium fluoride and spodumene. [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Calculated Li K peak position E, FWHM and intensity for the three compounds Li, LiF and spodumene.

	Li	LiF	Spodumene
E (eV)	54.4	56.0	55.0
FWHM (eV)	1.6	2.1	2.7

in the peak positions and shape in the corresponding X-ray spectra. Figure 7 compares the Li K emission band in Li metal, LiF and spodumene. The spectra are normalized to their maximum. The conversion to the emitted photon energy scale requires the use of *1s* binding energy of Li from XPS: 54.78 eV for Li metal,²¹ 56.8 eV for LiF²² and 56.4 eV for spodumene.²³ For lithium metal, the x-ray emission peak emerges at 54.2 eV, while for lithium fluoride it is at 56.0 eV, whereas spodumene presents its maximum at 55.0 eV. Hence, Li K emission shifts toward higher energies by +1.8 eV for LiF and +0.8 eV for spodumene compared to Li metal. The appearance of a shoulder at an energy of 51 eV is characteristic of spodumene. The secondary peak is located toward low photon energies, absent for the metal, and arising from the LVB, shifts in energy depending on the electronegativity of the atom, O or F, associated to Li. The highest the electronegativity, the lowest the photon energy.

Table 1 presents a summary of the peak maximum positions with calculated FWHM and intensity. It is worth noting that XPS binding energies used here could be prone to error since LiF and spodumene are insulators. Indeed, the emission of secondary electrons from the insulating samples leads to charge effects in XPS which can cause the shift of the binding energies of the

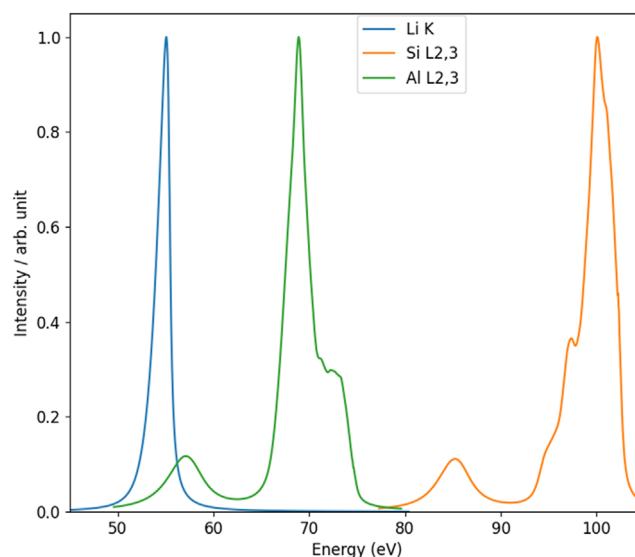


FIGURE 8 Li K (blue), Al L_{2,3} (green) and Si L_{2,3} (orange) emission bands of spodumene. [Colour figure can be viewed at wileyonlinelibrary.com]

core levels. For example, in the case of LiF, x-ray fluorescence spectroscopy using synchrotron radiation²⁹ revealed that Li K peak maximum should be at 46 eV, whereas with the chosen binding energy deduced by XPS²² this maximum falls at 56 eV.

One could think that the FWHM of the Li K emission band would be a good indication for the identification of the emitting material. Indeed, the three chosen materials have quite different band widths, ranging from 1.6 to 2.7 eV. However, let us note that the spodumene spectrum presents a large shoulder with a high intensity. We expect similar spectra for minerals having a crystalline structure close to the one of spodumene, where the shoulder could be a little more intense, thus leading to a much greater FWHM. So, this parameter alone should be used with caution, and the full shape of the emission band should rather be considered to identify the chemical state of lithium atoms.

3.5 | Possible interferences in the spectra of spodumene

From local and partial Al *sd* and Si *sd* DOS, we also calculated the L_{2,3} spectra (*3sd-2p* transitions) of aluminum and silicon in spodumene. Together with the Li K spectrum, the Al L and Si L spectra are placed on the same photon energy scale by using binding energies obtained from XPS²³: Li *1s* at 56.4 eV; Al *2p*_{3/2} at 74.6 eV; Si *2p*_{3/2} at 102.3 eV. The spectra are normalized to their maximum in Figure 8. The Li K spectrum interferes with the secondary peak of Al L_{2,3} centered at around 57.5 eV.

This will lead to difficulties in detecting and quantifying Li in spodumene. The Si $L_{2,3}$ emission does not interfere with the other spectra. However, if a wavelength dispersive spectrometer is used, then following the Bragg law or the grating law, the second diffracted order of the Si L emission will fall around a photon energy of 50 eV, interfering with the Li K emission. The FWHM of the Li K, Al $L_{2,3}$ and Si $L_{2,3}$ are 1.56, 2.66 and 3.38 eV respectively.

4 | CONCLUSION

This study has shown that the energy position and shape of the Li K emission band, as obtained by ab initio calculation with DFT, are strongly dependent on the structure and composition of the compounds. Indeed, the Li K spectrum reflects the energy distribution of the occupied Li p valence states within the valence band. Thus, the clear distinction in the shape and position of the spectra is due to the change in chemical state of lithium atoms. We also identified possible interferences that should be taken into consideration in the detection and quantification experiments and that could be problematic with lithium compounds containing oxygen and silicon.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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