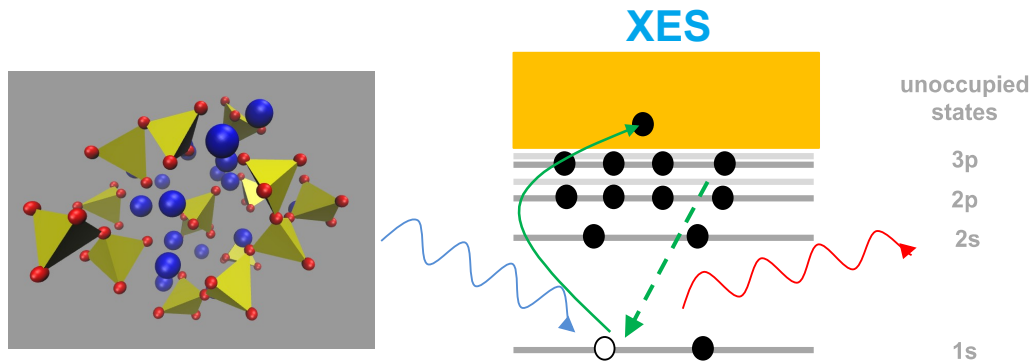


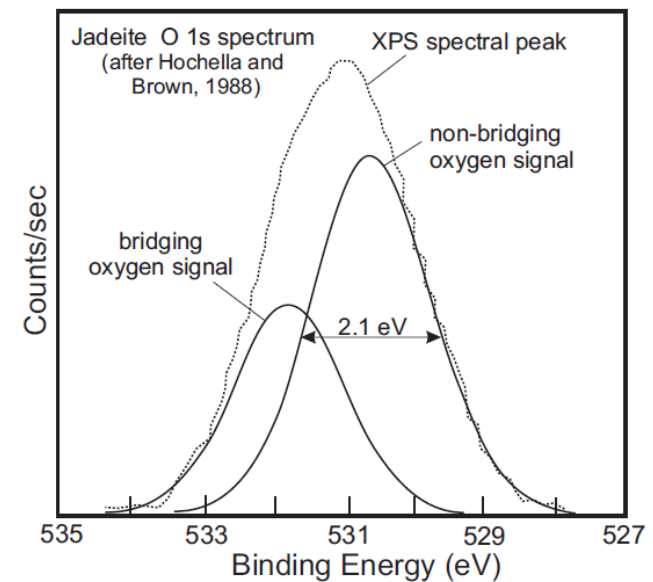
XPS-like evaluation of valence-to-core X-ray emission spectra: The case of germanate glasses



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a) The number of methods available to investigate the polymerization of germanate glasses (studied as structural analog of silicate glasses) *in situ* in high-pressure cells or other confined environments is limited. A complementary method would be desirable.

b) X-ray photoelectron spectroscopy (XPS), probing e.g. the oxygen 1s binding energy, is a *in-vacuum* direct method to access the difference in binding energy between bridging oxygen (BO) and non-bridging oxygen (NBO) atoms. See Figure on the right for a oxygen 1s XPS spectrum of NaAlSi₂O₆ jadeite. (Figure from Nesbitt et al. 2014 in RiMG)

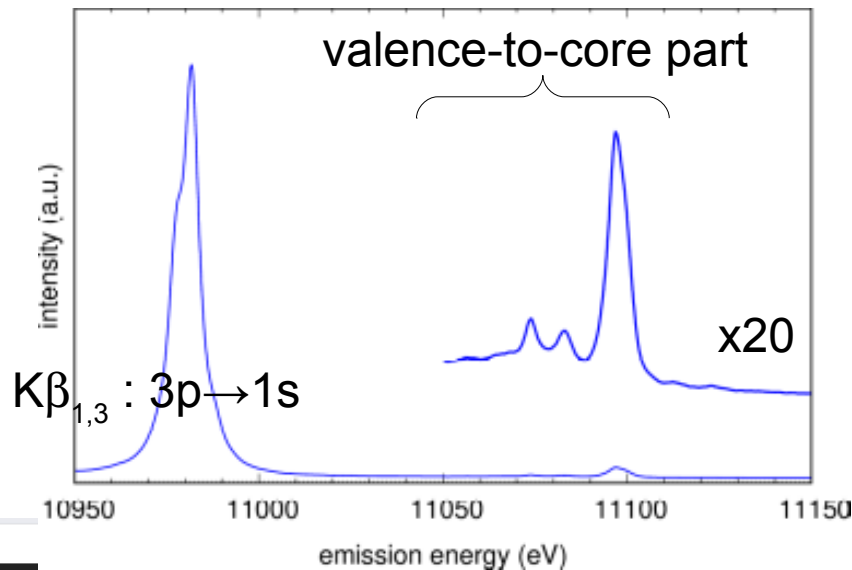


c) The oxygen 2s binding energies can be used for the same information.
Here valence-to-core X-ray emission spectroscopy (vtc-XES) comes into play!

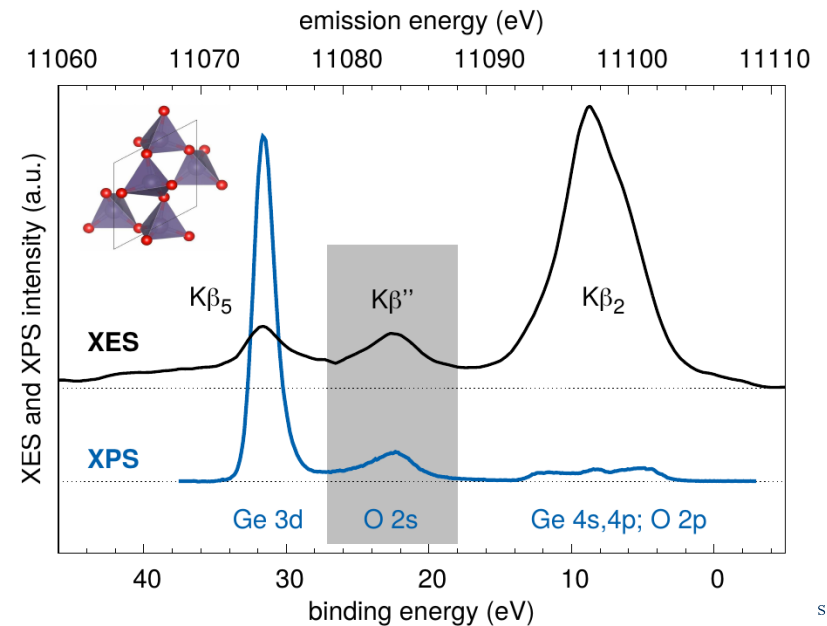
What does valence-to-core XES (vtc-XES) probe?

XES probes - practically speaking - the binding energy of occupied orbitals in any material by high-energy-resolution measurements of the characteristic element fluorescence lines, the same that are used in X-ray fluorescence analysis like in the EPMA. Vtc-XES records the binding energies of valence electrons, that have binding energies below 50 eV. With one important difference to XPS: The fluorescence signal from valence electrons in systems like germanates is **hard X-ray radiation, which does not need vacuum**.

This figure shows a typical XES spectrum of a germanate, with the vtc part magnified by x20. Note the X-ray photon energy on the x-axis.



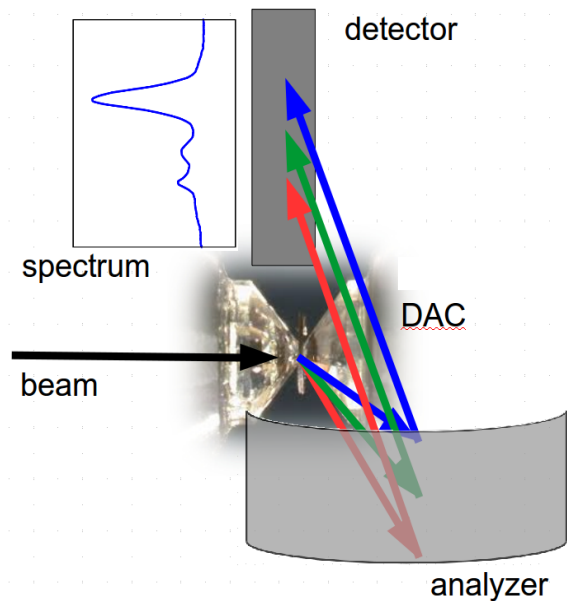
This figure shows a comparison of a XPS and a vtc-XES spectrum of quartz-like GeO_2 . The transition rules in XES lead to different relative peak intensities, but the energies are the same. Note the **oxygen 2s peak**.



How are valence-to-core XES spectra recorded?

Unfortunately, XES is 99% a synchrotron-based spectroscopy technique. Especially the valence-to-core signal is too weak to be recorded with laboratory X-ray sources.

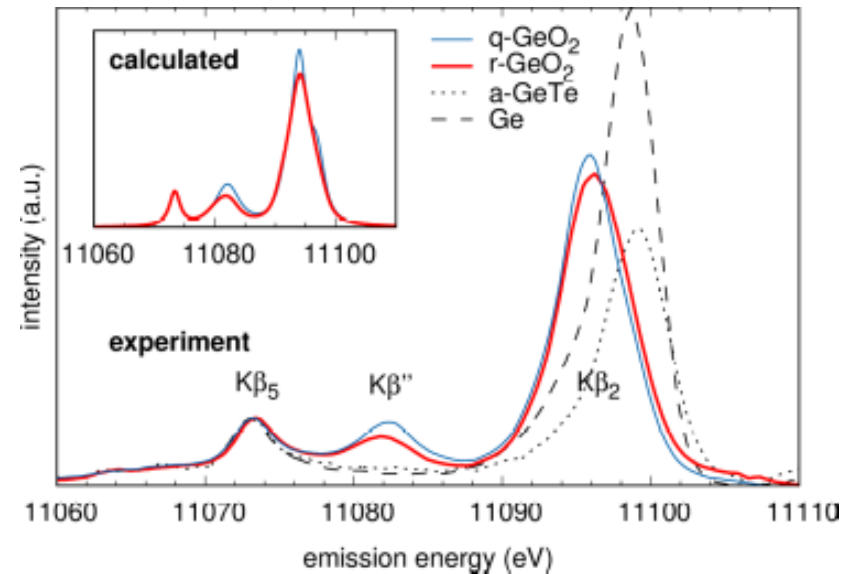
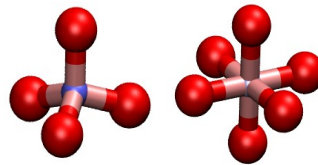
These figures show von-Hámos spectrometers, which are energy-dispersive by using cylindrically bent analyzer crystals and 2D detectors.



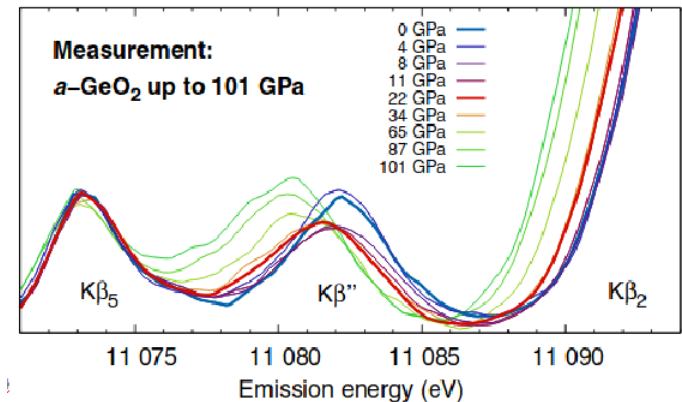
4x4 crystals at the European XFEL

The high sensitivity of the $K\beta''$ emission line

The oxygen 2s electron binding energy shows up in vtc-XES spectra as the so-called $K\beta''$ (spell: „K beta double-prime“). It is different by about 0.7 eV between quartz-like and rutile-like GeO_2 , which have germanium in fourfold and sixfold coordination, respectively.



Compressed amorphous GeO_2 in diamond anvil cells gradually increases coordination from four to six, which results in a remarkable shift (and intensity change) of the $K\beta''$. This coordination increase can be understood as a strong change in the first coordination shell. Both figures are from Spiekermann et al. 2019, Physical Review X, open source.



The past development of $K\beta''$ X-ray emission spectroscopy as a tool with which we can extract first-shell information on germanium in high-pressure applications was a team effort, that benefitted from careful reviewer comments. Here is the title and the list of my colleagues:

PHYSICAL REVIEW X **9**, 011025 (2019)

Persistent Octahedral Coordination in Amorphous GeO_2 Up to 100 GPa by $K\beta''$ X-Ray Emission Spectroscopy

G. Spiekermann,^{1,2,3,*} M. Harder,² K. Gilmore,⁴ P. Zalden,⁵ Ch. J. Sahle,⁴ S. Petitgirard,⁶ M. Wilke,¹ N. Biedermann,^{1,5}
C. Weis,⁷ W. Morgenroth,⁸ J. S. Tse,⁹ E. Kulik,² N. Nishiyama,^{2,10} H. Yavaş,^{2,11} and C. Sternemann⁷

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¹⁰*Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan*

¹¹*Linac Coherent Light Source, SLAC National Accelerator Laboratory,
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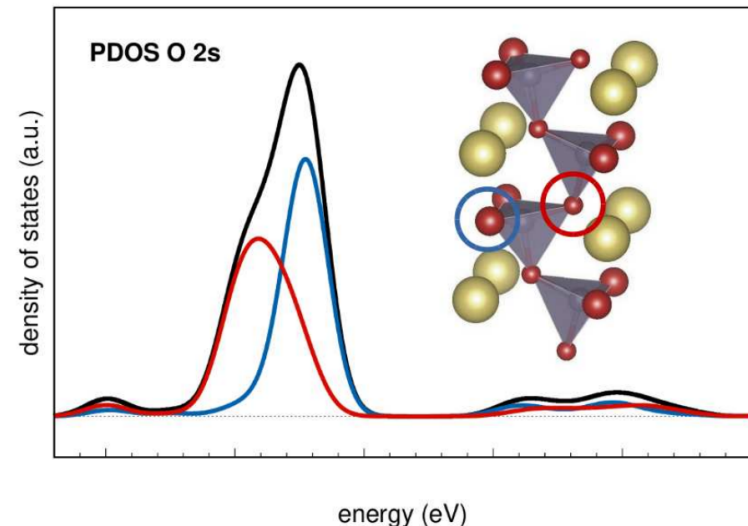
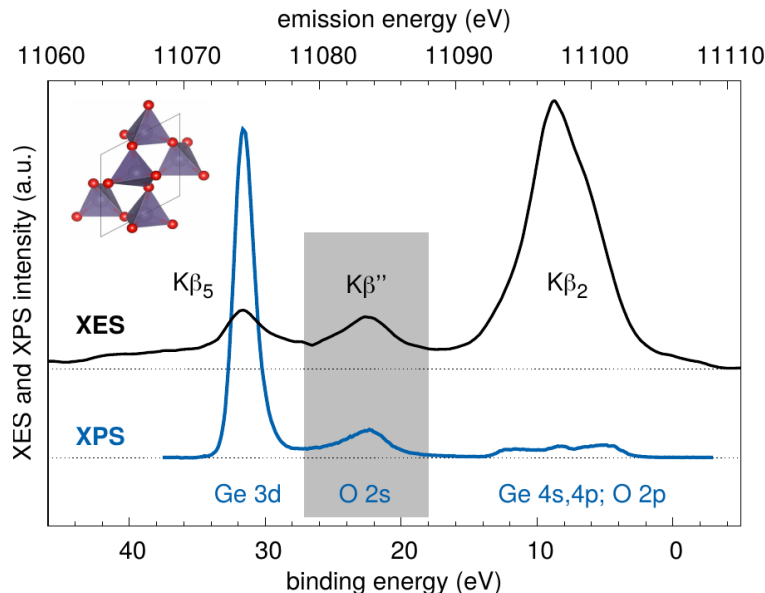
The ongoing development of $K\beta''$ X-ray emission spectroscopy as a tool with which we can extract second-shell information is what I am presenting now.

$K\beta''$ reflects the network polymerization in germanates

Figure left: The oxygen 2s electron binding energy shows up in germanium vtc-XES spectra as the so-called $K\beta''$ (spell: „K beta double-prime“).

Figure right: DFT calculations of a germanate pyroxene structure show that the overall projected density-of-states of oxygen 2s (black line) is composed of the different binding energy contributions from bridging (red) and non-bridging oxygen (blue).

This motivates the question: Will the $K\beta''$ emission line shift, when we measure germanate glasses with gradually increasing amount of non-bridging oxygen? (see next slide)



$K\beta''$ reflects the network polymerization in germanates

When we measure germanate glasses and crystals from pure quartz-like GeO_2 to olivine-like CaMgGeO_4 , the $K\beta''$ emission line shifts to lower binding energies, because of the increase in non-bridging oxygen atoms.

This shift amounts to 0.7 eV, a value clearly to resolve in XES spectra (left inset).

At the same time, the width of the $K\beta''$ emission line passes through a maximum, where the amounts of BO and NBO are equal.

Conclusion:

With some more effort, this effect may be turned into a probe of the germanate network polymerization in low-pressure diamond anvil cell experiments or other confined environments like solutions, furnaces etc.

No need of vacuum due to the high energy of X-ray photons.

