Journal of Electron Spectroscopy and Related Phenomena 184 (2011) 313–317

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

A soft X-ray approach to electron–phonon interactions beyond the Born–Oppenheimer approximation

M. Beye [a,*], A. Föhlisch [a,b]

[a] *Institute for Methods and Instrumentation in Synchrotron Radiation Research G-I2, Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Str. 15, 12489 Berlin, Germany*
[b] *Fakultät für Physik und Astronomie, Universität Potsdam, Karl-Liebknecht-Strasse 24-25, 14476 Potsdam, Germany*

ARTICLE INFO

Article history:
Available online 31 December 2010

Keywords:
Electron–phonon coupling
Resonant inelastic X-ray scattering
X-ray emission spectroscopy
Near edge X-ray absorption fine structure

ABSTRACT

With modern soft X-ray methods, the whole field of electron–phonon interactions becomes accessible directly in the ultrafast time domain with ultrashort pulsed X-ray sources, as well as in the energy domain through modern highly resolving spectrometers. The well-known core-hole clock approach plays an intermediate role, resolving energetic and temporal features at the same time. In this perspective paper, we review several experiments to illustrate the modern advances in the selective study of electron–phonon interactions as fundamentally determining ingredients for materials properties. We present the different complementary approaches that can be taken with soft X-ray methods to conquer this field beyond the Born–Oppenheimer approximation.

1. Introduction

The functionality of most materials is governed by the interplay of the nuclear and the electronic structure, whereas the static nuclear arrangement yields the potential energy surface in which the electronic structure is formed. Many dynamic processes, like phase transitions or basic chemical reactions, bond breaking and formation, are a consequence of a rearrangement of the nuclei and the formation of a new electronic structure alongside.

Nevertheless, in matter at standard conditions the nuclear arrangement is not static at all, but the nuclei vibrate around equilibrium positions due to thermal excitations at temperatures above the absolute zero. Quantized into phonons in solids, those vibrations affect the electronic structure, whereas the electronic structure itself is the force that drives the nuclei back into their equilibrium positions. Therefore, it is a natural consequence that electrons and phonons interact and their action is correlated. In certain cases, this correlation can lead to fascinating material properties, like e.g. superconductivity, following the BCS-theory [1].

The treatment of correlation effects with theoretical methods poses in general a big problem [2–4], whereas the different time and energy scales for the electronic and the phononic system allow a disentanglement in a Born–Oppenheimer approach [5], where the nuclear system is either taken to be static or the electrons follow instantly the nuclear rearrangements. Although this approximation has proven to be very successful, the strong excitation regime or a direct dynamic treatment is still a challenge.

It is a natural task for experiments to tackle the dynamics of electron–phonon interactions and the results of strong excitations. Applying soft X-ray techniques, we used distinct methods to address the fundamental processes in electron–phonon coupling in solid materials. In this article, we will review recent experiments that experimentally address this questions, whereas the organization is as follows:

In the first part of this paper, we will present how resonant inelastic X-ray scattering (RIXS) [6,7] and X-ray emission spectroscopy (XES) [8] together with thermal excitations of the phononic system up to the melting point can be used for quantitative studies of the electron–phonon interactions. Those interactions lead to a renormalization of the electron energies, characterized by a quasi-particle self-energy that can be split into a real part, reflecting the renormalization energy and an imaginary part, yielding a temporal information of the interaction [2]. In an approach similar to the core-hole-clock method [9,10], we use the core hole lifetime as an intrinsic clock to establish the temperature dependent rates for the transfer of crystal and even angular momentum in electron–phonon coupling events in the core excited system [11]. By using further information obtained with temperature dependent X-ray absorption spectroscopy (XAS), we can directly analyze how the thermally changed phononic excitation affects the electronic structure, changing the most prominent feature of a semiconductor – its band gap [12]. With this combined approach, we directly access both the real and imaginary part of the renormalization.

---

* Corresponding author. Tel.: +49 30 8062 14986.
E-mail address: martin.beye@helmholtz-berlin.de (M. Beye).

0368-2048/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.elspec.2010.12.032

By making use of the high resolution RIXS spectrometer SAXES [13] at the ADRESS beamline [14] at the Swiss Light Source, we study the vibrational progression in a molecular sample system in the electronic ground and excited states [15]. This directly maps out the potential energy surface of the involved electronic states even in the presence of vibrational and electronic correlation. Extending this study to solid state systems will lead to a direct map of the coupled electron–phonon potential energy surface in a highly dimensional configuration space.

As an outlook to future possible routes of soft X-ray spectroscopy to analyze electron–phonon couplings, we present how we study transient electronic structures with ultrafast XES at a novel soft X-ray light source [16]. We applied an optical excitation to excite nuclear rearrangements through electron–phonon coupling. We find that new phases of the material are transiently populated and that those phases can be straight-forwardly identified through their different electronic structures. With a more specific excitation source, we envision to resonantly excite phonons while we specifically study the electronic structure. This will provide the ultimate information about electron–phonon couplings in a very immediate experimental way [17].

2. Direct access to coupling rates

The specific selection rules of the photon-in photon-out techniques RIXS and XES allow to study the transfer of crystal and angular momentum. Without phonon coupling the photon energy in the excitation step in RIXS selects a specific crystal momentum that is conserved in the RIXS process. Only decays from the same point in *k*-space are observed [7]. The core excitation as well as thermal excitation lead to the formation of phonons. When an electron–phonon scattering event occurs during the lifetime of the core exited state, it becomes visible in decays that do not belong to the selected point in *k*-space. The spectral signature of decays with electron–phonon interactions mimics the Brillouin-zone averaged density of states because the coupling to phonons can randomly change the crystal momentum, whereas the energetic signature is only negligibly altered. The ratio of RIXS events with and without phonon scattering on the timescale of the core-hole lifetime is then directly related to the rate of crystal momentum transfer in electron–phonon scattering [11].

Turning to X-ray emission spectroscopy, the spectrum already reflects the Brillouin-zone averaged density of states without being disturbed by the *k*-selection rule encountered in RIXS. Here instead, the major difference to the calculated density of states is due to the dipole selection rule. The symmetry of the core hole determines the symmetry of the states that can be observed in radiative decays. The creation of phonons through the core excitation and through thermal excitation leads to electron–phonon scattering. When such an event transfers angular momentum during the core hole lifetime, this leads to decays that would have been selection rule forbidden without the coupling to phonons. In our case, we observe a growing admixture of symmetry forbidden decays with growing temperature.

We conducted the experiment at beamline UE52-PGM at BESSY II, Germany. At pressures below 10^{-9} mbar, we heated weakly B-doped Si (1 0 0) samples (specific resistivity >50 Ω cm) for several seconds above 1200 K to remove the surface oxide. Cleanliness was ensured by photoelectron spectroscopy. We recorded the spectra with a Scienta XES355 soft X-ray spectrometer [8]. The silicon sample was heated resistively and the temperature was recorded pyrometrically. The excitation bandwidth was set to 100 meV, whereas the soft X-ray spectrometer was operated at 400 meV resolution. For RIXS, we excited around the Si $L_{2,3}$ edge. XES was performed with excitation at 117 eV. The spectrometer was set to observe X-ray emission from valence states to the 2p levels.

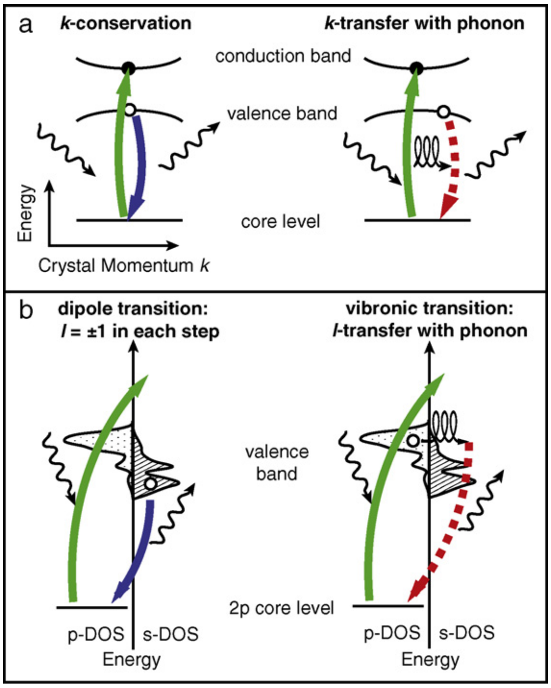

Fig. 1. (a) *k*-Conservation in RIXS (left): the incoming photons are resonantly absorbed at states with a specific *k*-vector (green). Only states with the same *k*-vector can decay (blue). Crystal momentum transfer due to electron–phonon scattering in RIXS (right): coupling to phonons opens additional decay channels for all states across the Brillouin zone. (b) *Left*: Electronic dipole transitions obey $\Delta l = \pm 1$. A 2p core-hole is created (green) and filled from valence s-states (blue). *Right*: The 2p core-hole can be filled from a valence p-state when a phonon with $|l| = 1$ is created or absorbed (curly line). The energy of the radiative transition (red) then reflects the p-DOS. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
Figure adapted from [11].

In Fig. 1, we present the physical processes underlying our study. From the RIXS spectra, we extract the ratio of recorded photons that reflect *k*-averaged and *k*-selective features. This ratio directly gives the product of the phonon scattering rate and the effective scattering duration time. The XES spectra have been fitted with a calculated density of states to extract the different ratios of the different symmetries to the measurement. This ratio is then numerically related to the angular momentum transfer in electron–phonon scattering. In Fig. 2, we plot the extracted phonon scattering rate as a function of temperature together with fits to the Bose-Einstein distribution function for an average phonon energy of 38 meV with a constant offset. This offset accounts for the temperature independent contribution of core hole induced phonons. We observe that per average phonon the crystal momentum is transferred with a rate of $0.20(2) \times 10^{15}\ \mathrm{s}^{-1}$ in electron–phonon scattering events, whereas the transfer rate of angular momentum is with $0.0035(4) \times 10^{15}\ \mathrm{s}^{-1}$ more than a factor of 50 slower.

3. Access to band renormalizations

To further gain access also to the real part of the renormalization self-energy, we study the band gap as a function of temperature. By using soft X-ray spectroscopy, we relate the band edges to the thermally unaltered Si 2p core level. With this method – in contrast to optical spectroscopy – we can separate the contributions to the renormalization stemming from the valence band or from the conduction band.

We use the above presented XES data and quantify the position of the valence band edge by fitting with an appropriate calculated