A Letters Journal Exploring
the Frontiers of Physics

OFFPRINT

Determining the electron-phonon coupling strength from Resonant Inelastic X-ray Scattering at transition metal L-edges

L. J. P. Ament, M. van Veenendaal and J. van den Brink

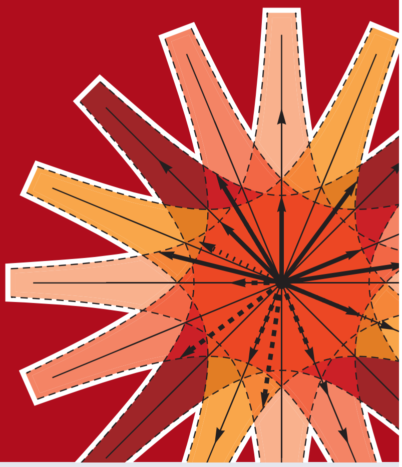
EPL, **95** (2011) 27008

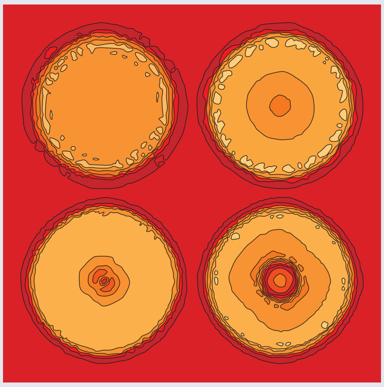
epl

A LETTERS JOURNAL EXPLORING THE FRONTIERS OF PHYSICS

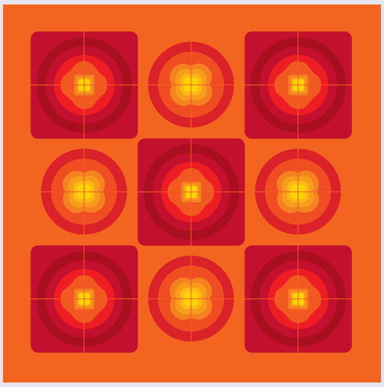
EPL Compilation Index

www.epljournal.org

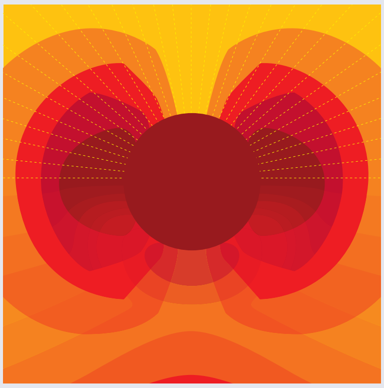




Biaxial strain on lens-shaped quantum rings of different inner radii, adapted from **Zhang *et al*** 2008 EPL **83** 67004.



Artistic impression of electrostatic particle–particle interactions in dielectrophoresis, adapted from **N Aubry and P Singh** 2006 *EPL* **74** 623.



Artistic impression of velocity and normal stress profiles around a sphere that moves through a polymer solution, adapted from **R Tuinier, J K G Dhont and T-H Fan** 2006 *EPL* **75** 929.

Visit the EPL website to read the latest articles published in cutting-edge fields of research from across the whole of physics.

Each compilation is led by its own Co-Editor, who is a leading scientist in that field, and who is responsible for overseeing the review process, selecting referees and making publication decisions for every manuscript.

- Graphene
- Liquid Crystals
- High Transition Temperature Superconductors
- Quantum Information Processing & Communication
- Biological & Soft Matter Physics
- Atomic, Molecular & Optical Physics
- Bose–Einstein Condensates & Ultracold Gases
- Metamaterials, Nanostructures & Magnetic Materials
- Mathematical Methods
- Physics of Gases, Plasmas & Electric Fields
- High Energy Nuclear Physics

If you are working on research in any of these areas, the Co-Editors would be delighted to receive your submission. Articles should be submitted via the automated manuscript system at **www.epletters.net**

If you would like further information about our author service or EPL in general, please visit **www.epljournal.org** or e-mail us at **info@epljournal.org**

EPS Società Italiana di Fisica EDP SCIENCES **IOP** Publishing

Image: Ornamental multiplication of space-time figures of temperature transformation rules (adapted from T. S. Bíró and P. Ván 2010 *EPL* **89** 30001; artistic impression by Frédérique Swist).

A Letters Journal Exploring the Frontiers of Physics

July 2011

EPL, **95** (2011) 27008
doi: 10.1209/0295-5075/95/27008

www.epljournal.org

Determining the electron-phonon coupling strength from Resonant Inelastic X-ray Scattering at transition metal L-edges

L. J. P. Ament[1,2], M. van Veenendaal[3,4] and J. van den Brink[2]

[1] *Institute-Lorentz for Theoretical Physics, Universiteit Leiden - 2300 RA Leiden, The Netherlands, EU*
[2] *Institute for Theoretical Solid State Physics, IFW Dresden - D-01171 Dresden, Germany, EU*
[3] *Department of Physics, Northern Illinois University - DeKalb, IL 60115, USA*
[4] *Argonne National Laboratory - 9700 S Cass Ave, Argonne, IL 60439, USA*

received 29 March 2011; accepted in final form 7 June 2011
published online 4 July 2011

PACS 78.70.Ck – X-ray scattering

Abstract – We show that high-resolution Resonant Inelastic X-ray Scattering (RIXS) provides direct, element-specific and momentum-resolved information on the electron-phonon (e-p) coupling strength. Our theoretical analysis indicates how the e-p coupling can be extracted from RIXS spectra by determining the differential phonon scattering cross-section. An alternative manner to extract the coupling is to use the one- and two-phonon loss ratio, which is governed by the e-p coupling strength and the core-hole lifetime. This allows the determination of the e-p coupling on an absolute energy scale.

Often novel electronic properties of a material can be understood by systematically unravelling the interaction between its electrons and phonons. Tunable electric transport properties in molecular crystals, for instance, are explained by the presence of a strong electron-phonon (e-p) coupling [1]. The dressing of electrons by phonons is also responsible for the colossal magnetoresistance effect in manganites [2]. More delicate is the role that the e-p interaction plays in high-T_c superconducting cuprates, a topic of a persisting debate [3–5]. The precise structure and strength of the e-p coupling is at the center this controversy. Here we show that high-resolution Resonant Inelastic X-ray Scattering (RIXS) gives direct, element-specific and momentum-resolved information on the coupling between electrons and phonons. We provide the theoretical framework required to distill e-p interaction strengths from RIXS, particularly in strongly correlated transition metal oxides such as the high-T_c cuprates.

In RIXS experiments, one scatters high-energy X-ray photons inelastically off a material [6]. The energy of the incident photons is chosen such that it coincides and thus resonates, with an intrinsic electronic excitation of the material under study —one of the material's X-ray absorption edges. At present the highest energy resolutions are reached at the L-edge of transition metal oxides, where an incident photon launches a $2p$ electron out of the atomic core into an empty $3d$ state around the Fermi-level. This highly unstable intermediate state decays rapidly, typically within 1–2 fs, so that the $2p$ core-state is refilled and an outgoing photon can be emitted. The state-of-the-art resolution is such that photon energy loss features on an energy scale of 25 meV can be distinguished at the copper or nickel L_3-edge [7–9].

This resolution has brought phonons within the energy window of observation and indeed last year for the first time phonon loss features were resolved in RIXS [8–10]. With the incident photons at the Cu L-edge having an energy of around 930 eV, this implies a resolving power better than 10^4. Advances in photon sources and instrumentation can further improve this. Here we show how the progress in accuracy allows the extraction of a number of characteristics of the e-p interaction directly from RIXS, including spatial information on the e-p coupling strength. Access to such e-p characteristics of strongly correlated systems, in particular $3d$ transition metal oxides, is of fundamental importance.

The advantage of RIXS is that during the scattering process the appreciable momentum carried by the photons can be transferred to the phonons in the solid, allowing the sampling of the phonon dispersion. Present methods to measure the e-p interaction do not have direct access to such $\mathbf{q}$-dependent information. Electron tunneling rates for instance, depend on momentum averages and one cannot easily select to measure the strength of the electron-phonon coupling at a given wave vector. An advantage is the high resolution available to electron transport measurements, rendering tunneling a very sensitive probe of (momentum averaged) e-p coupling constants for electrons close to the Fermi surface. On the other hand it is also intrinsically surface sensitive and confronted with the practical challenge to make good yet partially transparent barriers [11]. Such low-energy scales are not available to RIXS. An interesting feature of RIXS is however its element-specificity: in copper oxides phonons can for instance not only be accessed at the Cu L-edge, but also at the O K-edge —resolutions permitting.

A first phonon characteristic that is in principle accessible to RIXS is the phonon dispersion. Even if measuring it with RIXS is an interesting new utilization, one has to keep in mind that as a technique it is in this case up against very well-established methods such as inelastic neutron or (nonresonant) X-ray scattering. However, we wish to make the case here that what sets RIXS apart from, *e.g.*, neutron scattering is its capability to measure momentum-dependent e-p couplings. To formalize and elaborate on this statement, we start by introducing the e-p coupling Hamiltonian in generic form [12]:

$$H^{e-p} = \sum_{\mathbf{k},\mathbf{q},\lambda} M_{\mathbf{q}\lambda} d^\dagger_{\mathbf{k}-\mathbf{q}} d_{\mathbf{k}} (b^\dagger_{\mathbf{q}\lambda} + b_{-\mathbf{q},\lambda}). \qquad (1)$$

The Hamiltonian couples with a strength $M_{\mathbf{q}\lambda}$ phonons with momentum $\mathbf{q}$ and branch index λ, which are created by the operator $b^\dagger_{\mathbf{q}\lambda}$, to electrons that are described by the fermionic operators $d^\dagger_{\mathbf{k}}$. The phonon dynamics are governed by the phonon Hamiltonian $H^p = \sum_{\mathbf{q},\lambda} \omega_{\mathbf{q}\lambda} b^\dagger_{\mathbf{q}\lambda} b_{\mathbf{q}\lambda}$.

For definiteness we focus on the cuprates which have filled Cu $3d$ states apart from a single hole in the x^2-y^2 orbitals, but the analysis presented here is more general [13]. In the Cu L-edge RIXS process, the x^2-y^2 state is transiently occupied as an electron from the core is excited into it. As mentioned above, the filled x^2-y^2 state is short lived and quickly decays again. There is then a certain probability that after the decay process a phonon is left behind in the final state. Obviously this probability is related to the coupling of the x^2-y^2 electron to this particular phonon. Note that the presence of the core-hole ensures that the intermediate state is locally charge neutral. The phonons that couple to the $3d$ x^2-y^2 quadrupolar charge moment appear as loss-satellites in L-edge RIXS. Not all phonon modes couple equally to the RIXS intermediate state. To understand how the electron-phonon coupling is precisely reflected in the RIXS intensity we evaluate the RIXS amplitude for phonon scattering $A_{\mathbf{q}}$ from the Kramers-Heisenberg equation [14] $A_{\mathbf{q}} = \sum_n \frac{\langle f|\hat{D}|n\rangle\langle n|\hat{D}|i\rangle}{\omega_{\text{det}} - E_n + i\Gamma}$, where ω_{det} is the detuning energy of the incident photons from the L-edge resonance and E_n is the energy of intermediate state n with respect to the resonance. The initial, intermediate and final states are $|i\rangle$, $|n\rangle$ and $|f\rangle$ and the momentum loss of the photons in the scattering process is $\mathbf{q}$. The dipole operators $\hat{D} \sim \mathbf{p}\cdot\mathbf{A}$ in the scattering amplitude first create a $3d$ electron out of the localized $2p$ core-state and then annihilate it. Without polarization details we can denote it as $\hat{D} = \sum_{\mathbf{R}} (e^{-i\mathbf{k}_{\text{in}}\cdot\mathbf{R}} d^\dagger_{\mathbf{R}} p_{\mathbf{R}} + e^{i\mathbf{k}_{\text{out}}\cdot\mathbf{R}} d_{\mathbf{R}} p^\dagger_{\mathbf{R}})$. An important quantity is the inverse core-hole lifetime Γ, which determines the ultra-fast 1–2 fs time scale for the RIXS process. With this the RIXS scattering intensity becomes $I(\mathbf{q},\omega_{loss}) = \sum_f |A_{\mathbf{q}}|^2 \delta(\omega_{loss} - E_f + E_i)$, where ω_{loss} is the energy lost by the photon in the scattering process and E_i and E_f are the initial and final state energies, respectively.

It is well known that due to the presence of the intermediate states, it is in general impossible to evaluate RIXS scattering intensities exactly, even in model systems. One therefore often resorts to finite-size cluster calculations to compute RIXS spectra [15,16]. The e-p scattering problem at hand, however, is an exception. It can be solved exactly by means of canonical transformations. The fact that we are dealing with harmonic bosons allows for such a solution. We start by considering the limit of the coupling to an optical Einstein phonon and subsequently generalize to multiple dispersive phonons.

Einstein phonon. – For a local, nondispersive Einstein phonon the e-p Hamiltonian reduces to $H = \sum_{\mathbf{R}} M d^\dagger_{\mathbf{R}} d_{\mathbf{R}} (b^\dagger_{\mathbf{R}} + b_{\mathbf{R}}) + \sum_{\mathbf{R}} \omega_0 b^\dagger_{\mathbf{R}} b_{\mathbf{R}}$. This Hamiltonian can be diagonalized by a canonical transformation [12] $\bar{H} = e^S H e^{-S}$, with $S = \sum_{\mathbf{R}} S_{\mathbf{R}}$ where $S_{\mathbf{R}} = d^\dagger_{\mathbf{R}} d_{\mathbf{R}} \frac{M}{\omega_0} (b^\dagger_{\mathbf{R}} - b_{\mathbf{R}})$. As there is a single core-hole present, this results in $\bar{H} = \sum_{\mathbf{R}} \omega_0 b^\dagger_{\mathbf{R}} b_{\mathbf{R}} - \frac{M^2}{\omega_0}$, where the last term merely shifts the energy at which the resonance occurs. The phonon eigenstates are all the possible occupations $\{n_{\mathbf{R}}(m)\}$ of the phonon states with energies $E_m = \sum_{\mathbf{R}} n_{\mathbf{R}}(m)\omega_0 - M^2/\omega_0$. The eigenstates $|\bar{\psi}_m\rangle$ of $\bar{H}$ are related to the eigenstates $|\psi_m\rangle$ of H by $|\psi_m\rangle = e^{-S}|\bar{\psi}_m\rangle$. Inserting this transformation into the scattering amplitude $A_{\mathbf{q}}$ gives

$$A^{\text{Einstein}}_{\mathbf{q}} = \sum_m \frac{\langle f|\hat{D}e^{-S}|\bar{\psi}_m\rangle\langle\bar{\psi}_m|e^S\hat{D}|i\rangle}{\omega_{\text{det}} - E_m + i\Gamma}$$

$$= \sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}} \sum_{n_{\mathbf{R}}=0}^{\infty} \frac{\langle n'_{\mathbf{R}}|e^{-S_{\mathbf{R}}}|n_{\mathbf{R}}\rangle\langle n_{\mathbf{R}}|e^{S_{\mathbf{R}}}|n^0_{\mathbf{R}}\rangle}{z + M^2/\omega_0 - n_{\mathbf{R}}\omega_0}, \qquad (2)$$

with $z = \omega_{\text{det}} + i\Gamma$ and $n^0_{\mathbf{R}}$, $n_{\mathbf{R}}$ and $n'_{\mathbf{R}}$ are the occupations in the ground, intermediate and final states, respectively. The transferred momentum $\mathbf{q} = \mathbf{k}_{\text{in}} - \mathbf{k}_{\text{out}}$ springs from the dipole operators. The Franck-Condon overlap factors in the numerator can be evaluated exactly and are conveniently expressed in the functions $B_{mn}(g) = (-1)^m \sqrt{e^{-g} m! n!} \sum_{l=0}^{n} \frac{(-g)^l \sqrt{g}^{m-n}}{(n-l)! l! (m-n+l)!}$, with $g = M^2/\omega_0^2$. The RIXS amplitude to excite n' phonons when starting from the ground state is

$$A^{\text{Einstein}}_{\mathbf{q}} = \sum_{n=0}^{\infty} \frac{B_{\max(n',n),\min(n',n)}(g) B_{n0}(g)}{z + (g-n)\omega_0}. \qquad (3)$$

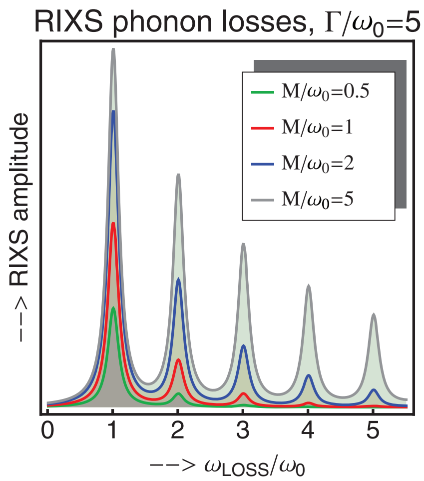


Fig. 1: (Colour on-line) Resonant Inelastic X-ray Scattering amplitude for phonon loss for Einstein phonon with energy ω_0 for different values of the dimensionless electron-phonon coupling M/ω_0. The inverse core-hole lifetime of $\Gamma/\omega_0 = 5$ is a typical value at the copper L-edge. The RIXS amplitude is evaluated at the incident energy that corresponds to the maximum in the X-ray absorption signal.

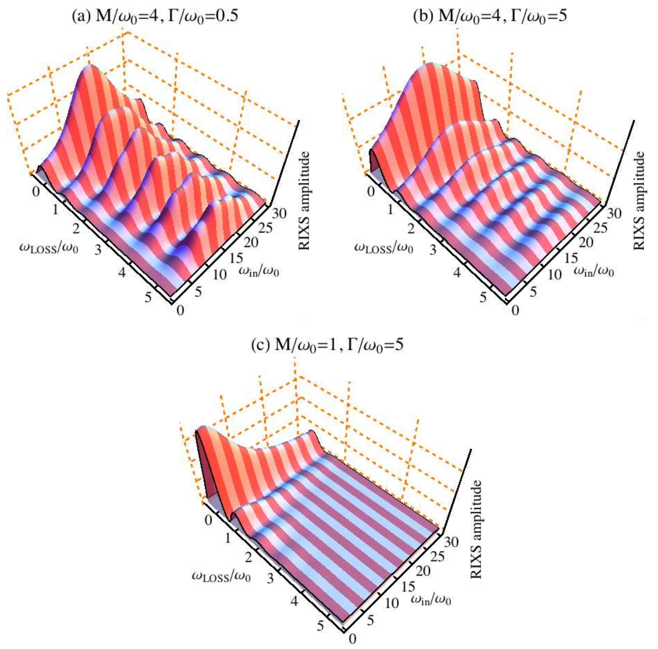


Fig. 2: (Colour on-line) Calculated RIXS amplitude for phonon loss as a function of loss energy ω_{loss} and incident energy $\omega_{in} = \omega_{det} + M^2/\omega_0$ in the case of (a) strong coupling and very long core-hole lifetime, (b) strong e-p coupling and (c) intermediate/weak e-p coupling.

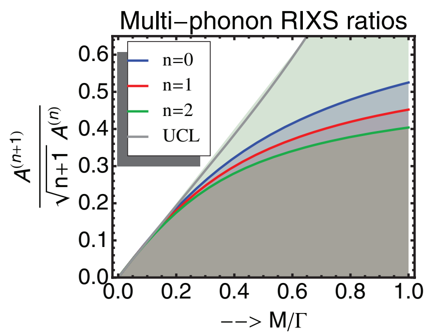


Fig. 3: (Colour on-line) Relation of the multiple phonon resonant RIXS amplitude to the electron-phonon coupling strength M/Γ. The ratio of the $n+1$ phonon $A^{(n+1)}$ to n phonon $A^{(n)}$ loss amplitudes is shown. Γ is the inverse core-hole lifetime. In the physical relevant regime these curves do not depend on the phonon frequency ω_0. The UCL expansion (straight gray line) gives accurate results for $M/\Gamma \lesssim 0.2$.

The resulting RIXS spectra for a typical weak, intermediate and strong coupling case are shown in figs. 1 and 2. It is clear that for stronger e-p interactions, a larger number of multi-phonon satellites carry appreciable weight. However, the first important observation is that the amplitude of the zero-loss peak $A^{(0)}$ is absolutely dominant (see fig. 2). This is even so in the strong e-p coupling regime, as long as $M/\Gamma < 1$. As at the Cu L_3-edge $\Gamma = 280\,\text{meV}$ [17], this corresponds to the physical situation, where typical phonon energies are of the order $\omega_0 = 30$–$100\,\text{meV}$. The coupling constant is determined by the phonon self-energy $M = \sqrt{\varepsilon_p \omega_0}$. Usual phonon self-energies are of the order of a few hundred meV, giving a coupling constant of the order of several tenths of a meV, which is smaller than the typical core-hole lifetime broadening. This observation is empirically supported by the fact that a dispersion of magnon [8] and bimagnon [18–20] excitations have been observed in L- and K-edge RIXS. Such dispersion cannot be present if these magnetic excitations are always accompanied by (multiple) phonon excitations that carry away momentum.

The exact amplitude for exciting a single phonon in the RIXS process is $A^{(1)} = (e^{-g}/\sqrt{g}) \sum_{n=0}^{\infty} g^n (n - g)/[n!(z + (g-n)\omega_0)]$. In leading order in the e-p coupling constant this amplitude is $A^{(1)} = M/z^2$. The differential single-phonon RIXS scattering amplitude $A^{(1)}$ is therefore directly proportional to the e-p coupling constant M, see fig. 3. By increasing z and thus tuning away from the absorption edge the scattering amplitude is reduced.

Dispersive phonons. – In close analogy with eq. (2), the case of multiple dispersive phonon modes can also be solved exactly. The scattering amplitude is

$$A_{\mathbf{q}} = \sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}} \times \sum_m \left[\frac{\prod_{\mathbf{k},\lambda} \langle n'_{\mathbf{k}\lambda}| \, e^{-S_{\mathbf{R}\mathbf{k}\lambda}} \, |n_{\mathbf{k}\lambda}(m)\rangle \, \langle n_{\mathbf{k}\lambda}(m)| \, e^{S_{\mathbf{R}\mathbf{k}\lambda}} \, |n^0_{\mathbf{k}\lambda}\rangle}{z + \sum_{\mathbf{k},\lambda} [g_{\mathbf{k}\lambda} - n_{\mathbf{k}\lambda}(m)]\omega_{\mathbf{k}\lambda}} \right], \tag{4}$$

where $n^0_{\mathbf{k}\lambda}$, $n_{\mathbf{k}\lambda}$ and $n'_{\mathbf{k}\lambda}$ are the occupation numbers of the modes indexed by $\mathbf{k}$ and λ in the ground, intermediate and final states, respectively. The sum over m is over all intermediate state occupations. Together with the Franck-Condon factors this constitutes a closed expression for the RIXS response.

UCL approximation. – Even when the e-p coupling g is not small, one can obtain the RIXS amplitude in approximate form by using the fact that the time scale of a typical phonon ($80\,\text{meV} \sim 52\,\text{fs}$) is much slower than the ultra-short RIXS time scale (1.6 eV $\sim 2.6\,\text{fs}$ at the Cu K-edge). This separation of time scales suggests that the scattering process contains a viable expansion parameter, which is small even for a fast phonon. The Ultra-short Core-hole Lifetime (UCL) expansion formalizes this observation [21,22]. In the present case it boils down to an expansion of the Kramers-Heisenberg expression in terms of $M_{\mathbf{q}\lambda}/\Gamma$. With the UCL expansion we obtain a compact, approximate expression for the phonon scattering amplitude that is also valid at finite temperature. In the case of dispersive phonons, eq. (4) is expanded as

$$A_{\mathbf{q},UCL} \approx \frac{1}{z}\sum_{\mathbf{R}} e^{i\mathbf{q}\cdot\mathbf{R}} \prod_{\mathbf{k},\lambda} \sum_{n_{\mathbf{k}\lambda}=0}^{\infty} \langle n'_{\mathbf{k}\lambda}|\, e^{-S_{\mathbf{R}\mathbf{k}\lambda}}\, |n_{\mathbf{k}\lambda}\rangle \times \langle n_{\mathbf{k}\lambda}|\, e^{S_{\mathbf{R}\mathbf{k}\lambda}}\, |n^0_{\mathbf{k}\lambda}\rangle \sum_{l=0}^{\infty} \left((n_{\mathbf{k}\lambda} - g_{\mathbf{k}\lambda})\omega_{\mathbf{k}\lambda}/z\right)^l, \quad (5)$$

where $S_{\mathbf{R}\mathbf{k}\lambda} = d^\dagger_{\mathbf{R}} d_{\mathbf{R}} \frac{M_{\mathbf{k}\lambda}}{\omega_{\mathbf{k}\lambda}} e^{i\mathbf{k}\cdot\mathbf{R}} (b^\dagger_{-\mathbf{k}\lambda} - b_{\mathbf{k}\lambda})$ and $g_{\mathbf{k}\lambda} = |M_{\mathbf{k}\lambda}/\omega_{\mathbf{k}\lambda}|^2$. The finite temperature comes in as an incoherent summation (*i.e.* after squaring $A_{q,UCL}$ in eq. (5)) of the different occupations $n^0_{k\lambda}$, weighted by a Boltzmann factor. As z is large compared to the phonon and e-p energy scales, we retain the leading terms in l and find the inelastic RIXS amplitude,

$$A^{(1)}_{\mathbf{q},UCL} = \frac{M_{\mathbf{q}\lambda}}{z^2} \langle f|\, b^\dagger_{\mathbf{q}\lambda} + b_{-\mathbf{q},\lambda}\, |i\rangle\,, \quad (6)$$

to first order in $M_{\mathbf{k}\lambda}/z$. Again, multi-phonon contributions to $A_{\mathbf{q}}$ are suppressed proportional to $M_{\mathbf{k}\lambda}/\Gamma$. This result implies that momentum-dependent RIXS can directly map out the $\mathbf{q}$-dependence of the e-p coupling strength $M_{\mathbf{q}\lambda}$. From this information for instance the spatial range of the e-p interaction $M_{\mathbf{r}\lambda}$ can be determined as it is directly related to the Fourier transform of $M_{\mathbf{q}\lambda}$.

RIXS provides still another method to extract e-p coupling strengths, which is expected to be particularly powerful in the case of weakly dispersive optical phonons, for instance modes around $80\,\text{meV}$ in the high-T_c cuprates [23,24]. From the UCL expansion one finds that the ratio of the one and two-phonon loss amplitude also directly reflects the e-p coupling constant: $A^{(2)}/A^{(1)} = \sqrt{2}M/z$. This is confirmed by the exact solution, for $M/\Gamma \ll 1$, see fig. 3. For strongly dispersive phonons this method also works if both $A^{(1)}_{\mathbf{q}}$ and $A^{(2)}_{\mathbf{q}}$ are measured throughout the Brillouin zone.

We note that since RIXS is a two-step process, one is dealing with matrix elements of the incoming and outgoing photoelectrons that can in principle be frequency dependent. But as the intensity of the single- and double-phonon loss features are compared at a fixed incoming photon energy, the matrix element for the absorption is not relevant. The outgoing matrix elements can be frequency dependent, but the change in photon energy is tenths of meV on several hundreds of electron volts. The relative change of the matrix elements as a function of frequency is therefore expected to be very small.

In the analysis above we concentrated on transition metal L-edge RIXS, which has the advantage of a photoelectron launched directly into the $3d$ state. A certain $3d$ orbital can be selected by choosing the polarization of incident and outgoing X-rays [25,26], so that e-p characteristics related this particular $3d$ orbital can be measured [8]. It is straightforward to include d-d excitations that couple to breathing and Jahn-Teller phonons [27], which are directly relevant in the study of Jahn-Teller polarons. Also at the O K-edge phonons can be probed but as this edge is at lower energy, the photons have less momentum and a smaller part of the Brillouin zone can be probed, which also holds for Cu M-edges. As hard X-ray transition metal K-edges do not suffer this disadvantage they do provide in principle a viable method to measure extensively momentum-dependent phonon properties and e-p interactions [10,28].

The simplification for the case of cuprates is that there is only one particular local configuration for the d electrons in the intermediate state ($3d^{10}$). For other $3d$ elements, one needs to take into account the different orbitals. For example, for a transition metal compound in octahedral symmetry, the e_g and t_{2g} orbitals will couple differently to the phonons. The occupation of these orbitals depends on the intermediate state that is excited. The RIXS intensities then can provide information on this coupling.

The framework presented here to extract the e-p coupling interaction shows how RIXS can provide direct, element-specific and momentum-resolved information on the interaction between electrons and phonons on an absolute scale. In weakly correlated electron systems these properties can be computed with modern *ab initio* electronic structure methods, for instance in the newly discovered iron pnictide superconductors [29] and the present framework to distill them from RIXS will allow for a direct comparison. In strongly correlated materials, particularly the high-T_c cuprates, high-resolution RIXS has the potential to become a unique tool to unravel the interaction between electrons and high energy phonon modes of particular symmetry.

* * *

We thank L. Braicovich, J. Hill, S. Johnston and T. Devereaux for fruitful discussions. This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences under contract DE-AC02-76SF00515 and by the Dutch "Stichting voor Fundamenteel Onderzoek der Materie" (FOM). MvV was supported by the U.S. Department of Energy (DOE), No. DE-FG02-03ER46097. Work at Argonne National Laboratory was supported by the U.S. DOE, Office of Basic Energy Sciences (BES), under contract No. DE-AC02-06CH11357. This research benefited from the RIXS Collaboration supported by the Computational Materials Science Network (CMSN), BES, DOE under grant No. DE-FG02-08ER46540.

REFERENCES

[1] Hulea I. N., Fratini S., Xie H., Mulder C. F., Iossad N. N., Rastelli G., Ciuchi S. and Morpurgo A. F., *Nat. Mater.*, **5** (2006) 982.

[2] Millis A. J., Littlewood P. B. and Shraiman B. I., *Phys. Rev. Lett.*, **74** (1995) 5144.

[3] Lanzara A., Bogdanov P. V., Zhou X. J., Kellar S. A., Feng D. L., Lu E. D., Yoshida T., Eisaki H., Fujimori A., Kishio K., Shimoyama J.-I., Noda T., Uchida S., Hussain Z. and Shen Z.-X., *Nature*, **412** (2001) 510.

[4] Giustino F., Cohen M. L. and Louie S. G., *Nature*, **452** (2008) 975.

[5] Reznik D., Sangiovanni G., Gunnarsson O. and Devereaux T. P., *Nature*, **455** (2008) E6.

[6] Ament L., van Veenendaal M., Devereaux T., Hill J. P. and van den Brink J., *Rev. Mod. Phys.*, **83** (2011) 705.

[7] Ghiringhelli G., Piazzalunga A., Dallera C., Schmitt T., Strocov V. N., Schlappa J., Patthey L., Wang X., Berger H. and Grioni M., *Phys. Rev. Lett.*, **102** (2009) 027401.

[8] Braicovich L., Ament L., Bisogni V., Forte F., Aruta C., Balestrinoi G., Brookes N., de Luca G., Medaglia P., Miletto Granozio F., Radovic M., Salluzzo M., van den Brink J. and Ghiringhelli G., *Phys. Rev. Lett.*, **102** (2009) 167401.

[9] Braicovich L., van den Brink J., Bisogni V., Moretti Sala M., Ament L., Brookes N., De Luca G., Salluzzo M., Schmitt T. and Ghiringhelli G., *Phys. Rev. Lett.*, **104** (2010) 077002.

[10] Yavas H., van Veenendaal M., van den Brink J., Ament L., Alatas A., Leu B., Apostu M., Wizent N., Behr G., Sturhahn W., Sinn H. and Alp E., *J. Phys.: Condens. Matter*, **22** (2010) 485601.

[11] Allen P., *Handbook of Superconductivity* (Academic Press, New York) 1999, p. 478.

[12] Mahan G. D., *Many-Particle Physics* (Springer-Verlag, New York) 2000.

[13] Ament L., van Veenendaal M. and van den Brink J., in preparation.

[14] Blume M., *J. Appl. Phys.*, **57** (1985) 3615.

[15] Kotani A. and Shin S., *Rev. Mod. Phys.*, **73** (2001) 203.

[16] van Veenendaal M., *Phys. Rev. Lett.*, **96** (2006) 117404.

[17] Krause M. O. and Oliver J. H., *J. Phys. Chem. Ref. Data*, **8** (1979) 329.

[18] Hill J. P., Blumberg G., Kim Y.-J., Ellis D. S., Wakimoto S., Birgeneau R. J., Komiya S., Ando Y., Liang B., Greene R. L., Casa D. and Gog T., *Phys. Rev. Lett.*, **100** (2008) 097001.

[19] van den Brink J., *EPL*, **80** (2007) 47003.

[20] Forte F., Ament L. J. P. and van den Brink J., *Phys. Rev. B*, **77** (2008) 134428.

[21] van den Brink J. and van Veenendaal M., *Europhys. Lett.*, **73** (2006) 121.

[22] Ament L. J. P., Forte F. and van den Brink J., *Phys. Rev. B*, **75** (2007) 115118.

[23] d'Astuto M., Mang P. K., Giura P., Shukla A., Ghigna P., Mirone A., Braden M., Greven M., Krisch M. and Sette F., *Phys. Rev. Lett.*, **88** (2002) 167002.

[24] Padilla W. J., Dumm M. and Basov D. N., *Phys. Rev. B*, **72** (2002) 205101.

[25] Kuiper P., Guo J.-H., Sathe C., Duda L.-C., Nordgren J., Pothuizen J. J. M., de Groot F. M. F. and Sawatzky G. A., *Phys. Rev. Lett.*, **80** (1998) 5204.

[26] Ament L., Ghiringhelli G., Moretti Sala M., Braicovich L. and van den Brink J., *Phys. Rev. Lett.*, **103** (2009) 117003.

[27] van den Brink J., *Phys. Rev. Lett.*, **87** (2001) 217202.

[28] Hancock J. N., Chabot-Couture G. and Greven M., *New J. Phys.*, **12** (2010) 033001.

[29] Boeri L., Dolgov O. V. and Golubov A. A., *Phys. Rev. Lett.*, **101** (2008) 026403.