Influence of Source Coherence on X-Ray Absorption Spectroscopy

J. Hunter Dunn,[1,*] D. Arvanitis,[1] R. Carr,[2] and N. Mårtensson[1]

[1]*Department of Physics, University of Uppsala, Box 530, S-751 21 Uppsala, Sweden*

[2]*Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Stanford University, Stanford, California 94309*

(Received 13 July 1998)

Core-level x-ray absorption spectroscopy measurements have been performed at the $L_{3,2}$ edges of Fe and Co thin films. The degree of source coherence was varied using soft x rays from five different beam lines. We observe an increase of the L edge resonance intensities relative to the continuum states which we propose is due to the presence of transverse coherence in the exciting radiation.

PACS numbers: 78.70.Dm, 78.90.+t

Synchrotron radiation is widely used as an excitation source in a variety of spectroscopic experiments. The relevance of the transverse coherent character of the light has been demonstrated in imaging [1] and in structural and dynamic studies [2–5]. In these measurements the presence of transverse coherence is evident via interference effects. In this Letter, we propose that transverse coherence is also of importance in x-ray absorption spectroscopy (XAS). We find that applying established XAS analysis procedures results in the intensity of the white lines at the L_3 and L_2 edges of Fe and Co thin films being enhanced when using light with a degree of transverse spatial coherence. This spectroscopic observation is highly relevant, not only in the discussion of free electron lasers specifically designed to produce high brightness, high flux coherent radiation [6], but also for third generation synchrotron sources already running at, or near, the diffraction limit.

The experiments were performed using SX700 beam lines at the BESSY synchrotron facility in Berlin, Germany [7], beam line 22 at the MAX laboratory in Lund, Sweden [8], the Super-ESCA beam line at the Elettra facility in Italy [9], beam line 1.1 at the SRS synchrotron facility in Daresbury, United Kingdom [10], and beam line 5.2 at the SSRL, Stanford, California [11,12]. At BESSY, MAX-lab, and the SRS dipole magnet radiation was used. At Elettra and SSRL the x rays are produced by undulators. In the latter case, an elliptically polarizing undulator enables the polarization state of the light to be varied [11].

The energy resolution and calibration at BESSY and SSRL was monitored *in situ* from measurements of the absorption yield from the $M_{4,5}$ edges of La in a $LaAl_2$ crystal. The La M_5 resonance ($h\nu \approx 835$ eV) at the SX700 III beam line at BESSY had a full width at half maximum (FWHM) of 1.86 eV indicating a resolution, ΔE, of 1.7 eV for a 50 μm exit slit. For beam line 5.2 at SSRL a FWHM of 1.7 eV at 835 eV was achieved with a 20 μm exit slit yielding a Gaussian contribution of 1.5 eV. These figures give a *longitudinal* coherence length, $\frac{\lambda^2}{\Delta\lambda}$, of ≈ 1 μm in each case. To enable a comparison of the spectral features we have used the established analysis procedures for normalization of XAS spectra over the continuum step. This involves subtraction of a constant background from the pre-edge region of the spectra which are then normalized to the same value using the high energy continuum step. This procedure is based on the fact that, with the exception of the weak extended x-ray absorption fine structure oscillations in this region, the height of the continuum step in XAS is proportional to the cross section of the isolated atom [13,14]. In addition, this process effectively removes unwanted spectral contamination that originates from both stray light and higher orders of both the grating and, where appropriate, the source. In Fig. 1 a nonlinear $M_{4,5}$ resonance intensity increase relative to the small continuum step is already evident as the exit slit opening is reduced and the degree of *transverse* coherence increased. The enhancement is far in excess of any effect that may be attributed to an improvement in resolution alone.

The monochromator of beam line 5.2 at SSRL uses both entrance and exit slits in a Rowland circle geometry. A

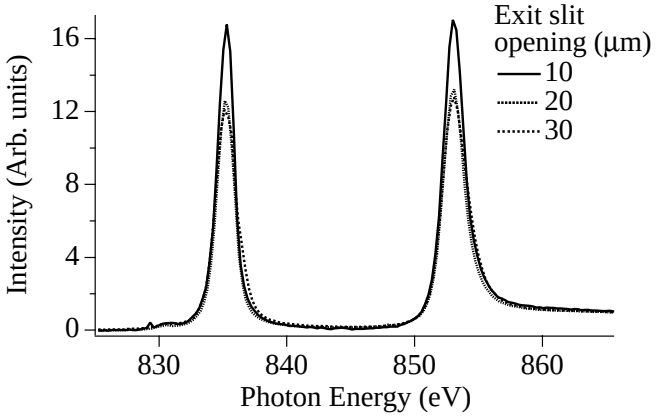

FIG. 1. The lanthanum $M_{4,5}$ edges from a $LaAl_2$ crystal used to calibrate the beam line energy and resolution at BESSY and SSRL. The resolution is of order 1.5 eV at the La M_5 edge for beam line 5.2 at SSRL. Linear x-ray light was used. The x rays were at 90° to the crystal surface. The spectra have been normalized to a constant pre-edge to post-edge continuum jump of unity to allow ready comparison. The peak height relative to the continuum is seen to increase as the exit slit is closed and the available light becomes partially transversely coherent. This increase is not commensurate with any appreciable increase in resolution since the FWHM remains almost constant for all the slit settings.

50 μm entrance slit was used. Calculating the diffraction pattern of the entrance into the exit slit shows that for exit slit openings below 20 μm, for the energies of interest here, predominantly the central diffraction maximum will reach the sample. Thus, reducing the exit slit below 20 μm results in only a marginal improvement of energy resolution (or longitudinal coherence) of the incident x rays. The data of Fig. 1 confirm that the energy resolution is limited at small exit slit openings.

To ensure the highest possible sample quality all thin film samples were prepared and measured *in situ* in ultrahigh vacuum. In addition to low energy electron diffraction and Auger electron spectroscopy, the magnetic properties of these films have been used to critically verify that preparation at different facilities produced samples that appear to be identical. The preparation procedures and magnetic measurements have been reported previously [13,14]. A monodomain magnetic response was obtained, highlighting the high quality and single crystalline character of the samples. XAS was performed in the electron yield mode using electron detectors and by simultaneously measuring the sample drain current. Both detection channels agreed extremely well.

In the case of magnetic systems, XAS spectra may be used to obtain information on the orbital and spin moments of the photoexcited atom [15]. This procedure necessitates a precise intensity analysis of XAS features as well as the use of circular and linear x rays. A higher degree of coherence appears to result in a relative enhancement of the resonance features. This could explain discrepancies in derived magnetic moments from measurements made at different synchrotron facilities.

For any monochromatic electromagnetic source, a degree of transverse coherence may be extracted when viewed through a sufficiently small aperture. By sampling a small enough region of the source, phase information is retained over neighboring optical paths leading to a wave front with a degree of coherence. Based on diffraction theory, the degree of coherence in the image plane of an extended, incoherent quasimonochromatic source may be calculated [16]. A macroscopic coherence length of illumination at the sample may be achieved when the greatest optical path difference between the exit slit and sample, Δx, is much less than the wavelength, λ. For the L and M edges presented here $\lambda \approx 17$ Å. In terms of geometrical optics, a necessary condition for this may be expressed as

$$\Delta x = \frac{a^2}{2x} \ll \lambda , \qquad (1)$$

where $2a$ is the exit slit opening and x is the distance between the exit slit and sample.

From Eq. (1), we conclude that the radiation from the SX700 II and III beam lines at BESSY and beam line 22 at MAX-Lab has no significant transverse coherence when using a 50 μm exit slit. This is largely due to the small distance between the exit slit and sample in these beam line configurations. At SSRL partial coherence is evident when using a 20 μm exit slit in combination with the fixed exit slit to sample distance of 7 m. Partial coherence is similarly predicted at the Super-ESCA beam line with an exit slit opening of 30 μm and a distance to sample of 3.6 m. The geometric result of these parameters is to predict a macroscopic area of coherent illumination on the sample. For beam line 5.2 at SSRL we have derived this length from Fresnel diffraction measurements. We found the coherence area to be of order 23 μm^2. Under similar experimental conditions coherent x rays have been observed at other undulator beam lines [1–3,5]. Despite a similarly large average exit slit to sample distance of 3.2 m at beam line 1.1 of the SRS, an exit slit opening of 400 μm was used preventing any preservation of phase over the different possible optical paths. This discussion is summarized in Table I.

Illustrating the effect of transverse coherence, Fig. 2 shows dichroic Fe L edge absorption spectra from body centered cubic (bcc) Fe films measured at the various facilities. For incoherent sources the spectra coincide except at those photon energies where dichroic effects are expected due to the differing degree of circular polarization of the x rays. Note that in these cases the intensity of the L_3 and L_2 resonances is modified in the *opposite* direction. In the case of the partially coherent source, while the dichroic intensity is further increased due to the very high degree of circular polarization, more obvious is the increase of the L_3 and L_2 resonances in the *same* direction by a factor of about 1.6. This translates to a 20% increase in the integrated area below these spectral features once the continuum edge has been removed. A similar enhancement is presented in Fig. 3 for a face centered tetragonal (fct) Co/Cu(100) thin film. Here linearly polarized x rays were used. The degree of transverse coherence was varied by reducing the exit slit opening as in the case of the La $M_{4,5}$ spectra shown in Fig. 1.

The presence of stray light has been explicitly addressed in the cases of Daresbury and SSRL using filters with tailored energy cutoffs. No evidence could be found that

TABLE I. Comparing the various beam lines used in preparation of this work. $2a$ is the exit slit opening and x is the distance between the exit slit and sample. The last column shows the optical path difference over x as derived from simple optical theory. In each case the difference, Δx, should be compared with λ ($\approx$17 Å), the wavelength of the soft x rays used for the L edge absorption measurements.

Beam line	a (μm)	x (m)	Δx (Å)
BESSY SX700 III	25	0.2	15.6
MAX-lab BL 22	25	0.2	15.6
Elettra Super-ESCA	15	3.6	0.38
SRS BL 1.1	200	3.2[a]	66.6
SSRL BL 5	10	7	0.32[b]

[a]Exit slit moves during scan.
[b]Coddling slit.

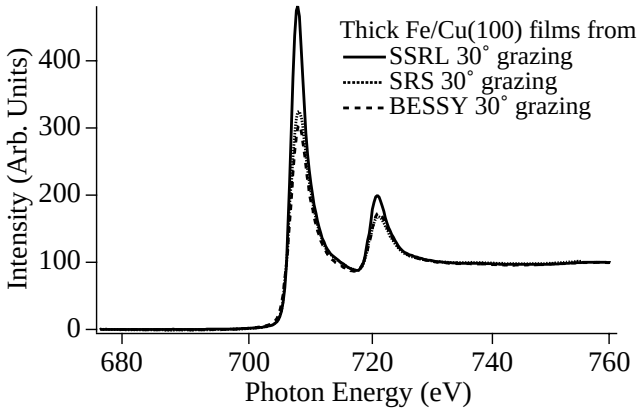

FIG. 2. The $L_{2,3}$ edges of a 20 atomic layer Fe film prepared on the (100) surface of a Cu crystal measured using circular light. The resonant features show a marked increase in intensity and area at facilities where the beam line provides a degree of transverse coherence. The pre-edge to post-edge continuum jump has been normalized 100 units to allow ready comparison of the spectra. With the magnetization in the surface plane, different x-ray incidence angles were used. This allows saturation effects to be accounted for. A similar enhancement was found in spectra taken with the opposite helicity. These curves are omitted here for clarity.

linked the observed spectral enhancement to such optical effects. Higher order contributions are intrinsically eliminated in the case of beam line 5.2 due to the undulator high energy cutoff and rapidly decreasing beam line transmission above 1600 eV effectively removing the onset of the next undulator harmonic. For each experiment, the linearity of the detected signal versus photon flux was checked. The enhancement of spectral lines is observed when reaching a regime of partial transverse coherence by reducing the opening of the exit slit alone (Figs. 1 and 3). We therefore propose that this phenomenon is of a more fundamental nature, originating from the interaction of the x-ray light with the electronic degrees of freedom of the target.

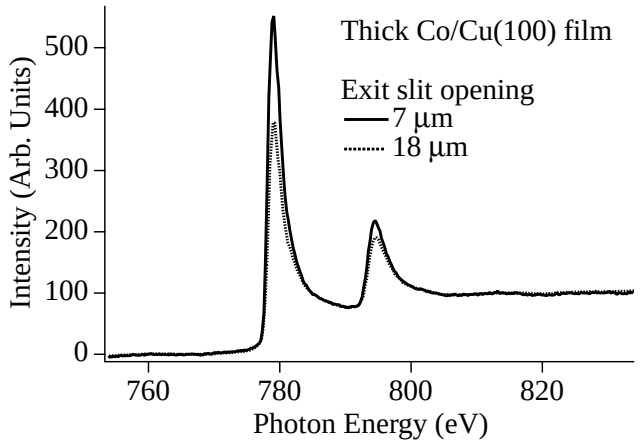

FIG. 3. The $L_{2,3}$ edges of a 20 atomic layer cobalt film exhibit an increase in the resonance intensity relative to the continuum edge jump as the exit slit is reduced. Changes in the FWHM are negligible while the integrated area under the curves increases. The spectra have been normalized to an edge jump of 100 units. Linearly polarized x rays at normal incidence were used.

Support for the observations presented above is found in recent scattering experiments using partially coherent x rays [2,4,5]. Such measurements are sensitive to both the real and imaginary components of the scattering factor, $f(E)$. In these experiments effects due to transverse source coherence have been documented. For example, in the presence of disorder, characteristic "speckle" features have been observed. Under these conditions, any description of the scattered intensity I requires the phase information to be retained. In doing so cross amplitude terms arising from the different scatterers may no longer average to zero but contribute to the scattered intensity.

The total energy dependent scattering factor is often written

$$f(E) = f_0 + f'(E) + if''(E), \tag{2}$$

where f_0 is the energy independent part of the scattering factor. $f'(E)$ is the real part and $f''(E)$ the imaginary part of the dispersion at energy E. In an absorption experiment, such as XAS, $f''(E)$ may be written

$$f''(E) = \frac{mcE}{2e^2h}\,\sigma(E), \tag{3}$$

where $\sigma(E)$ is the absorption cross section, measured here by means of electron yield. The appropriate Kramers-Kronig transform may then be used to write Eq. (2) purely in terms of the absorption cross section. Hard x-ray diffraction measurements have documented the nonlocal response when measuring I with coherent light [3,4]. That $f'(E)$ and $f''(E)$ are complementary components of the same phenomena has been substantially verified both experimentally and theoretically [17]. Finally, anomalous dispersion is strongest at absorption edges and it is therefore natural to expect any intensity variations to exhibit a strong energy dependence. Given these considerations, it is not surprising that transverse coherence influences the relative spectral intensities in absorption spectroscopy.

Because of the complexity of resonant excitation with x-ray light, the usual assumption in XAS literature is based on an "ideal" photon source, the light from which consists of monochromatic plane waves, spatially infinite in extent. Given this assumption the problem may then be reduced to that of transition probabilities that are proportional to the absorption cross section. These probabilities may be calculated by considering only the electronic degrees of freedom of the system [18]. Within this framework, one mechanism that directly influences the spectroscopic process on length scales of the order of the transverse coherence area is the form of the electric field driving the transition. For coherent illumination, one approach would be to consider the total electric field at an atomic site, $\mathbf{E}_{\mathrm{tot}}$, as being a sum of the incident field, $\mathbf{E}_{\mathrm{in}}$, and the coherent dielectric response

field of the material, $\mathbf{E}_{di}$: $\mathbf{E}_{tot} = \mathbf{E}_{in} + \mathbf{E}_{di}$. The coherent dielectric response field modifies the electric field at the site of excitation leading to a possible enhancement of spectral features.

The white line intensity variations presented here are very similar for high quality films of bcc Fe (Fig. 2) and fct Co (Fig. 3) despite the fact that one is a strong and the other a weak ferromagnet. Not only do these films have different $3d$ occupation numbers, but also relative fillings in the minority versus majority exchange spin split subbands. Both circular and linear x-ray light were used in several geometries. In each case, the resulting spectra yielded similar intensity variations. These observations suggest that the phenomena observed here are more sensitive to the crystal structure, degree of order, and dielectric response than to finer details in electronic structure that lead to differences in magnetic properties. We note here that the high degree of crystallographic order for the *in situ* prepared thin films yields single crystalline domains of length scales similar to that which characterizes the transverse coherence of the source. The enhancement observed here for $LaAl_2$ is of a lesser extent (Fig. 1). It is not clear if this is due to the higher degree of crystallographic disorder in this case, differences in electronic structure, or simply to the different electronic symmetry of the initial state wave function.

The data presented here, with the above discussion, indicate the need for any model of the spectroscopic process to include a delocalized response of the solid within the coherence dimensions of the source. Such considerations have been made in the past for interband transitions with reference to L and M edge spectra [19], which were treated specifically later [20], using a delocalized electron theory. More recently, a theory of the absorption of ultraviolet light [21] predicted a delocalized response of the solid upon the creation of a core hole by considering a coupling between the core hole and valence electrons via an induced dynamic dipole field of the core electrons.

In conclusion, we have presented data that show how the degree of spatial coherence in synchrotron radiation based x-ray absorption spectroscopy modifies the relative intensity of near edge resonance features. This is supported by scattering experiments, the relation of which to absorption measurements is given via Kramers-Kronig transforms.

The authors thank Jeff Moore of SSRL and the excellent support offered by the facility staff. It is a pleasure to acknowledge enlightening discussions with Carl-Olof Almbladh, Kwang-Je Kim, and Sebastian Doniach. This work was supported by the Swedish Natural Science Research Council. Experiments at BESSY, Elettra, and SRS were supported by the European LSI program. The work of R. C. was supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. DE-AC03-76SF00515.

*Present address: Stanford Synchrotron Radiation Laboratory, Stanford Linear Accelerator Center, Stanford University, Stanford, CA 94309.

[1] J. Kirz, H. Ade, C. Jacobsen, C.-H. Ko, S. Lindaas, I. McNulty, D. Sayre, S. Williams, and X. Zhang, Rev. Sci. Instrum. **63**, 557 (1992).
[2] M. Sutton, S. G. J. Mochrie, T. Greytak, S. E. Nagler, L. E. Bergman, L. E. Held, and G. B. Stephenson, Nature (London) **352**, 608 (1991).
[3] S. Brauer, G. B. Stephenson, M. Sutton, R. Brüning, E. Dufresne, S. G. J. Mochrie, G. Grübel, J. Als-Nielsen, and D. L. Abernathy, Phys. Rev. Lett. **74**, 2010 (1995).
[4] I. K. Robinson, R. Pindak, R. M. Fleming, S. B. Dierker, K. Ploog, G. Grübel, D. L. Abernathy, and J. Als-Nielsen, Phys. Rev. B **52**, 9917 (1995).
[5] M. Altarelli, Solid State Commun. **102**, 199 (1997).
[6] D. Attwood, K. Halbach, and K.-J. Kim, Science **228**, 1265 (1985).
[7] H. Petersen, M. Willmann, F. Schäfers, and W. Gudat, Nucl. Instrum. Methods Phys. Res., Sect. A **333**, 594 (1993).
[8] J. N. Andersen, O. Björneholm, A. Sandell, R. Nyholm, J. Forsell, A. N. L. Thånell, and N. Mårtensson, Synchrotron Radiation News **4**, 15 (1991).
[9] A. Abrami *et al.*, Rev. Sci. Instrum. **66**, 1618 (1995).
[10] M. Surman *et al.*, Rev. Sci. Instrum. **63**, 4349 (1992).
[11] R. Carr, J. B. Kortright, M. Rice, and S. Lidia, Rev. Sci. Instrum. **66**, 1862 (1995).
[12] R. Carr and S. Lidia, in *Proceedings of the SPIE's International Symposium on Optics, Imaging and Instrumentation, San Diego, CA, 1993*, SPIE Proceedings Vol. 2013 (SPIE–International Society for Optical Engineering, Bellingham, WA, 1993), p. 56.
[13] J. Hunter Dunn, D. Arvanitis, N. Mårtensson, M. Tischer, F. May, M. Russo, and K. Baberschke, J. Phys. C **7**, 1111 (1995).
[14] J. Hunter Dunn, D. Arvanitis, and N. Mårtensson, Phys. Rev. B **54**, 11 157 (1996).
[15] P. Carra, B. T. Thole, M. Altarelli, and X. Wang, Phys. Rev. Lett. **70**, 694 (1993).
[16] M. Born and E. Wolf, in *Principles of Optics* (Pergamon Press, New York, 1959), Chap. 10.
[17] H. Stragier, J. O. Cross, J. J. Rehr, L. B. Sorensen, C. E. Bouldin, and J. C. Woicik, Phys. Rev. Lett. **69**, 3064 (1992).
[18] C.-O. Almbladh and L. Hedin, in *Handbook on Synchrotron Radiation*, edited by E. E. Koch (North-Holland Publishing Company, Amsterdam, 1983), Vol. 1; (private communication).
[19] G. D. Mahan, Phys. Rev. **163**, 612 (1967).
[20] P. Nozières, J. Gavoret, and B. Roulet, Phys. Rev. **178**, 1084 (1969).
[21] E. Zaremba and K. Sturm, Phys. Rev. Lett. **66**, 2144 (1991).