No multiatom resonances observed in x-ray fluorescence

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We present a study of the effects of interatomic multiatom resonant photoemission monitored by soft x-ray emission. The partial fluorescence yield of certain transitions F $K\alpha$ and C $K\alpha$ is measured while the excitation energy is scanned through the higher lying thresholds (La $M_{4,5}$ and Ti $L_{2,3}$, respectively) of the neighboring atoms in the multicomponent systems (LaF$_3$,Ti$_x$Nb$_{1-x}$C). No evidence for a resonant enhancement in the fluorescence signal as suggested by the multiatom resonant photoemission effect is found.

Soft x-ray fluorescence measurements have found great interest in the last ten years triggered by the development of powerful synchrotron radiation sources and efficient x-ray spectrometers and detectors.[1] Various phenomena have been studied by tuning the energy of exciting photons through the thresholds of the emitting atoms. The electronic structure (site-selective distribution of partial density of states[2–5] and band mapping),[4,5] the geometrical structure of atoms in adsorbates,[6,7] the phase composition in interfaces,[8] the local structure of impurities,[6] and new phenomena at the giant resonances[8,9] have been studied in detail. In all these cases the energy of the exciting photons is tuned through the threshold of emitting atoms. In the present paper, we analyze the effects arising in the x-ray fluorescence of selected emitting atoms when the excitation energy passes the higher thresholds of other neighboring constituent atoms of the multicomponent system.

The well-known *intra-atomic* resonant photoemission[10] takes place *within* the atom and leads to a resonant enhancement in the photoemission intensity of an outer shell when the excitation energy can excite an electron of a deeper lying shell. Recently, the *interatomic* multiatom resonant photoemission (MARPE) has been discovered which involves a number of different atoms. First measurements of this effect in metal oxides (MnO, Fe$_2$O$_3$, La$_{0.7}$Sr$_{0.3}$MnO$_3$) have been reported[11] and a theoretical model has been developed to describe the effects.[12] MARPE occurs when photon energy is tuned to a core-level absorption edge of an atom (Mn, Fe, or La) neighboring the emitting atom (O) with the emitting level (O $1s$) having a lower binding energy than the resonant level (Mn $2p$, Fe $2p$, or La $3d$). It has been suggested that enhanced photoemission from the O $1s$ core level involves a resonance with deeper-lying levels (Mn $2p$ and La $3d$). Energy-integrated effects of 11–29% were found.[11]

MARPE should be sensitive to bonding distances, bonding type, and magnetic order and would provide a direct way to determine near-neighbor atomic parameters. Therefore, it offers a broad variety of possible applications. Since the effect increases the number of core holes in the sample, it should be detectable via fluorescence or Auger decay. A recent study[13] presents experimental evidence for an enhanced decay of the primary core hole detected via fluorescence

emission (from MnO) and Auger electron emission (from Fe$_2$O$_3$). In Ref. 13, the O $K\alpha$ fluorescence signal in MnO decreases by about 88% of its prethreshold value when exciting at the Mn L_3 threshold, which is about a 7% stronger signal than the calculation predicts (95%), and has been considered evidence for the MARPE effect.

In this paper, we studied this effect in x-ray fluorescence. We measured the excitation-energy dependence of F $K\alpha$ x-ray emission spectra (XES) of LaF$_3$ near the La $3d$ thresholds and did not find any significant enhancement of the emitted intensity. An additional XES angle-dependent study of Ti$_x$Nb$_{1-x}$C confirmed our findings. Especially in consideration of the broad applicability claimed for MARPE, soft x-ray fluorescence is not a suitable technique to study such an effect.

Our measurements were performed at Beamline 8.0.1 of the Advanced Light Source, Lawrence Berkeley Laboratory. The undulator beamline is equipped with a spherical monochromator,[14] the resolving power has been set to $E/\Delta E = 1100$ for LaF$_3$ and to $E/\Delta E = 550$ for Ti$_x$Nb$_{1-x}$C. The emitted radiation is analyzed by a Rowland circle-grating spectrometer that provides a resolving power of about 540 at about 680 eV (for LaF$_3$) and 620 at 280 eV (for Ti$_x$Nb$_{1-x}$C). The angle between the incident beam and the spectrometer was fixed at 90° and the plane of incidence is in the plane of polarization. The absorption spectra were taken in the total electron yield (TEY) mode or in the sample current mode. The samples were a bulk of polycrystalline Ti$_x$Nb$_{1-x}$C and a crystal of LaF$_3$. All measurements were performed at room temperature. All experimental curves are displayed as measured without broadening or smoothing the data.

LaF$_3$ offers fluorine $K\alpha$ and lanthanum M_5N_3 emission peaks within a narrow energy range covered by our detector window and therefore both transitions can be monitored simultaneously. Figure 1 shows the F $K\alpha$ emission spectra taken at five excitation energies through the La $3d$ threshold. The measured absorption is shown in the top inset obtained in TEY. The three peaks arise from transitions between the ground state $3d^{10}4f^0$ (^1S) and the three terms of the $3d^94f^1$ configuration (^3P, ^3D, ^1P). When exciting at the M_4 and M_5 thresholds (solid curves) the emitted intensity in the

$FK\alpha$ (VB $2p\rightarrow 1s$ centered at 683.7 eV) strongly decreases and the La M_5N_3 ($4p_{3/2}\rightarrow 3d_{5/2}$ at 644.6 eV) emission intensity is increased due to the opening of the $3d$ excitation channel. The La $3d$-$4f$ resonance is known for its strong radiationless Coster-Kronig transitions[15] ($3d_{3/2}\rightarrow 3d_{5/2}$), which accounts for the fact that the M_5 ($3d_{5/2}$) emission occurs when exciting on the M_4 ($3d_{3/2}$) threshold.

In Fig. 2, the $FK\alpha$ partial fluorescence yield (PFY) for LaF$_3$ displayed. The fluorescence yield has been measured for an incidence angle of 50° to the sample surface. The detector window is narrowed to accept $FK\alpha$ photons (680–695 eV) only, and the excitation energy is scanned through the La $3d$-$4f$ threshold. Two minimums are observed that coincide with the La M_4 and M_5 thresholds. The $FK\alpha$ fluorescence decreases by about 90% when the excitation energy reaches the La $M_{4,5}$ thresholds. The reason for the decrease in general is that less incoming photons create F $1s$ core holes because the photons are directed towards the opening $3d$-$4f$ channels. The dashed curve corresponds to the calculation of the partial fluorescence yield.

In order to simulate the (partial) fluorescence emission from a certain transition while the excitation energy is tuned through a higher-lying threshold of a different compound, we used the following expression for the number of photons emitted by a sample that is thick (compared to the penetration depth of the exciting radiation):[16]

$$\frac{dN_{\text{PFY}}}{N_0 d\Omega} \propto \frac{(1-R)}{4\pi} \sum_{i,j} \omega_{i,j} \frac{{}^p\mu_i}{\mu}$$

$$\times \int_0^d \mu \exp\left(-\frac{\mu}{\sin\alpha} z\right)(1-R_{i,j})$$

$$\times \exp\left(-\frac{\mu_{i,j}}{\sin\beta} z\right) dz$$

$$\propto \sum_{i,j} \omega_{i,j} \frac{{}^p\mu_i}{\mu + \mu_{i,j}\tan\alpha} \propto \frac{1}{\mu + \mu_{i,j}\tan\alpha}.$$

In this equation, dN_{PFY} denotes the number of photons emitted by the sample of thickness d in the solid angle $d\Omega$. The radiation impinges at an angle of incidence α and the fluorescence is emitted at the angle β (both to the sample surface) such that $\alpha + \beta$ is constant. The indexes i,j describe the summation over all existing core holes i and their possible decay channels j. N_0 is the number of incident photons, μ is the total photo-absorption coefficient, and ${}^p\mu_i$ is the partial photoabsorption coefficient for the creation of a hole in shell i. The quantity $\mu_{i,j}$ is the absorption coefficient for the fluorescence radiation from the transition of level j to i with the fluorescence yield $\omega_{i,j}$. R and $R_{i,j}$ are the reflection coefficients for the incoming and outgoing radiation, respectively, for the interface vacuum sample and vice versa. This expression neglects Compton processes as well as the possible reemission of low-energy photons following possible self-absorption of the fluorescence radiation. This is reasonable for La M and F K shells where the Auger decay is dominating. The ratio ${}^p\mu_i\mu$ represents the probability for the creation of a hole in the shell i and the ratio $\mu/(\mu + \mu_{i,j})$ takes
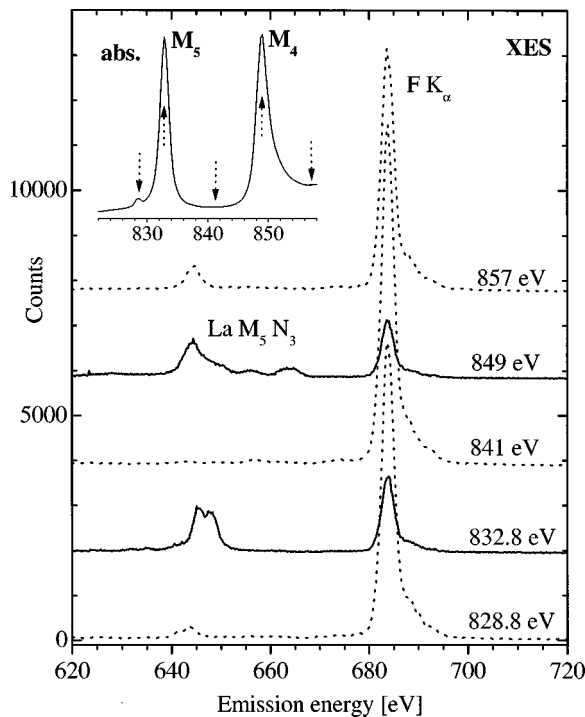

FIG. 1. Soft x-ray emission of LaF$_3$. The excitation energy is tuned through the La $3d$ threshold. The arrows in the absorption spectrum (shown in the inset) indicate the energies at which the $FK\alpha$ emission spectra are excited. Due to the onset of the La $3d$ channel, the $FK\alpha$ emission is diminished when the excitation energy is tuned to the $M_{4,5}$ thresholds.
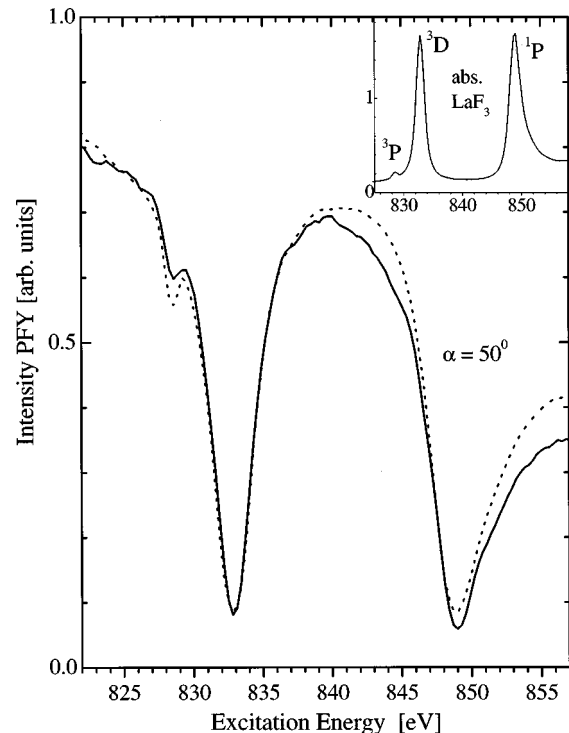

FIG. 2. Fluorine $K\alpha$ partial fluorescence yield (solid line) of LaF$_3$ for excitation through the La $3d$ resonances. The model calculation is plotted as dotted line.

the self-absorption of the emitted fluorescence radiation into account. The reflection of incoming and outgoing radiation is negligible ($R, R_i \ll 1$) as is the exponential term due to the thickness of the sample $[1/(\mu + \mu_{i,j}) \ll d)]$. The partial cross section $^p\mu_i$ far above threshold (O $1s$) is practically constant over the comparably small energy range of the partial fluorescence yield scans (for LaF$_3$, 822 to 857 eV). We have used the final term of Eq. (1) to estimate the partial fluorescence yields and it depends on the ratio $1/(\mu + \mu_{i,j} \tan \alpha)$. In order to compute the PFY, it is essential to obtain the correct (relative) total absorption spectrum $\mu(E)$ as well as the correct *ratio* of absorption coefficients $\mu_{i,j}$ to μ.

The (relative) absorption coefficient $\mu(E)$ is determined by our measurement (as shown in the inset of Figs. 1 and 2). In order to determine the ratio $\mu_{i,j}/\mu$, a second absorption spectrum has been measured that extends across both thresholds, the threshold of the fluorescence emission (F $K\alpha$ or C $K\alpha$) and the threshold of the excitation (La $M_{4,5}$ or Ti $I_{2,3}$, respectively). The ratio was determined experimentally to be $\mu_{i,j} = 0.63\mu(684\,\text{eV})$ for LaF$_3$ and $\mu_{i,j} = 1.32\mu(455\,\text{eV})$ for Ti$_x$Nb$_{1-x}$C. For comparison, the values obtained from Henke's atomic scattering factors[17] are 0.6 and 1.25, respectively. It turns out that these differences do not lead to a significant change in the calculated spectrum and therefore are negligible.

The crucial parameter for the calculation is the correct peak-to-background ratio in the measured absorption spectra. It is important to use the same resolving power of the exciting radiation when obtaining the partial fluorescence and the electron yield absorption spectra. For example, an increase in resolving power will result in an increase in the peak-to-background ratio of the absorption (and emission) spectrum, which ultimately enhances the contrast in the calculated curve. We have measured the absorption and the partial fluorescence emission spectra simultaneously. Due to the inherently low fluorescence yield count rates a moderate resolution has been chosen although the strong signal provided by the absorption measurement would allow for absorption spectra to be obtained at much higher resolution.

Although the fluorescence data of MnO in Ref. 13 were measured at the same beamline as our data, the way the absorption spectrum has been obtained was different from our case. In Ref. 13, the partial Mn $2p$ electron emission has been measured. This absorption spectrum was then brought to the scale of the total absorption by scaling with the Henke data. Finally, the spectrum was broadened in order to obtain the same experimental resolution as the one used in the fluorescence experiment.

In Fig. 2, the calculated curve matches the measured curve fairly well. In particular, the data do not show a larger fluorescence yield than the calculated curve and therefore do not indicate an increased number of F $1s$ holes due to a multiatom resonant interaction.

In Fig. 3 the C $K\alpha$ partial fluorescence yield for Ti$_x$Nb$_{1-x}$C is shown for three different angles of incidence ($\alpha = 15°$, 55°, and 75°). The excitation energy is scanned through the Ti $2p$ edge. In the inset, the Ti $2p$ absorption as used for the calculation is shown, and the extended absorption spectrum, including the carbon K edge. The arrows indicate where the ratio $\mu_{i,j}/\mu$ of 1.32 has been determined. From the data, we cannot conclude that the measured fluo-
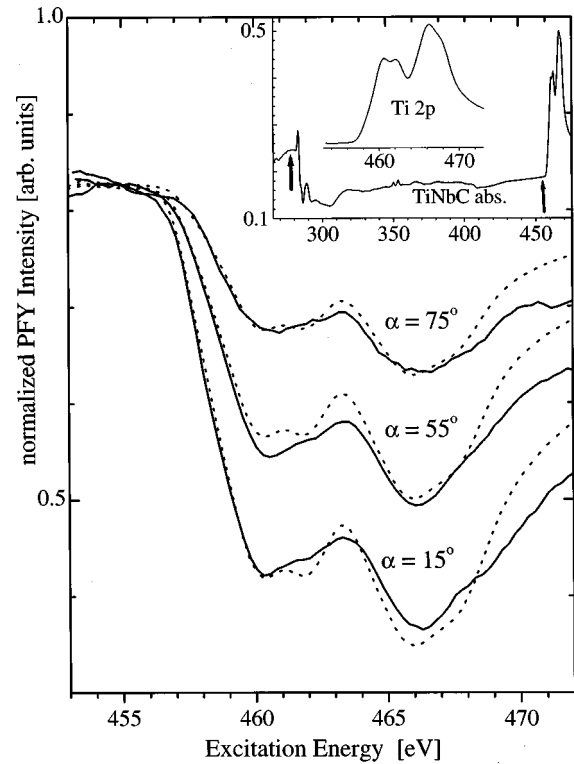

FIG. 3. Carbon $K\alpha$ partial fluorescence yield (solid line) of Ti$_x$Nb$_{1-x}$C. The excitation energy is scanned through the Ti $2p$ resonances.

rescence yield shows a greater fluctuation than the yield calculated from Eq. (1) using the absorption data. Such an observation would indicate an increased number of C $1s$ core holes due to a multiatom resonant effect. The largest deviation between measurement and calculation (at the Ti $2p$ peak) is about 3% in the sense that the measured fluorescence signal drops in the peak by 55%, and the calculated signal by 58%. Our measurements suggest that the MARPE effect would be at most a 3% effect. In addition, we find it difficult to obtain the correct peak-to-background ratio in the absorption with this same accuracy. It is not possible to conclude that the measured fluorescence is generally stronger than calculated, which would indicate an increased number of C $1s$ core holes due to a multiatom resonant effect. Apparently, the intensity of the calculated spectra for LaF$_3$ and Ti$_x$Nb$_{1-x}$C increases more rapidly than the measured curves once the high-energy threshold is passed. It is presently unclear what could account for this behavior, but it could be due to increasing nonradiative processes like Auger emission.

In most cases, a clean surface (by photoemission standards) is not required for x-ray emission experiments because the escape depth of the fluorescence photons is large compared to the thickness of the adsorbates that form a layer in the order of ~ 1 nm thick. Therefore, most of the fluorescence arises from the bulk of the sample. For the absorption measurement, surface contamination layers influence the spectrum more strongly due to the much smaller escape depth of the photoelectrons. We reduced the surface impurities by shining the intense zero-order beam of the monochromator on the sample. The photon stimulated desorption of

carbon impurities will lead to cleaning of the sample to some extent.[18] Annealing of the $Ti_xNb_{1-x}C$ did not produce an enhancement in the peak-to-background ratio of the absorption spectrum.

To summarize, we have monitored the partial fluorescence from certain transitions ($F K\alpha$ in LaF_3 and $C K\alpha$ in TiNbC) of one atom, while the excitation energy passes the (higher) thresholds ($La M_{4,5}$ and $Ti L_{2,3}$, respectively) of the neighboring atoms. We do not find any evidence for an enhancement in the number of fluorine and carbon core holes produced by the multiatom resonances, and therefore, no indication for the MARPE effect. Inherent difficulties such as the weak fluorescence signal and measurement of the correct peak-to-background ratio (clean sample, same resolving power for XES and x-ray absorption spectroscopy) lead us to the conclusion that fluorescence spectroscopy does not seem a suitable way to detect multiatom resonances especially with regard to routine and broad applications. Our results also indicate that the MARPE effect is much weaker (less than 3%) than suggested by previous authors.[11-13,19]

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[1] J. Nordgren and N. Wassdahl, Phys. Scr., T **31**, 103 (1991).

[2] S. M. Butorin, J.-H. Guo, N. Wassdahl, P. Skytt, J. Nordgren, Y. Ma, C. Ström, L.-G. Johansson, and M. Qvarford, Phys. Rev. B **51**, 11 915 (1995).

[3] E. Z. Kurmaev, S. Stadler, D. L. Ederer, Y. Harada, S. Shin, M. M. Grush, T. A. Callcott, R. C. C. Perera, D. A. Zatsepin, N. Ovechkina, M. Kasai, Y. Tokura, and T. Takahashi, Phys. Rev. B **57**, 1558 (1998).

[4] Y. Ma, N. Wassdahl, P. Skytt, J. Guo, J. Nordgren, P. D. Johnson, J.-E. Rubensson, T. Boske, W. Eberhardt, and S. D. Kevan, Phys. Rev. Lett. **69**, 2598 (1992).

[5] A. Nilsson, J. Electron Spectrosc. Relat. Phenom. **93**, 143 (1997).

[6] J. A. Carlisle, L. J. Terminello, E. A. Hudson, R. C. C. Perera, J. H. Underwood, T. A. Callcott, J. J. Jia, D. L. Ederer, F. J. Himpsel, and M. G. Samant, Appl. Phys. Lett. **67**, 34 (1995).

[7] E. Z. Kurmaev, S. Stadler, D. L. Ederer, Y. M. Yarmoshenko, D. A. Zatsepin, M. Neumann, T. A. Callcott, M. M. Grush, R. C. C. Perera, S. E. Danilov, and V. L. Arbuzov, Mater. Trans., JIM **39**, 570 (1998).

[8] A. Moewes, T. Eskildsen, D. L. Ederer, J. Wang, J. McGuire, and T. A. Callcott, Phys. Rev. B **57**, R8059 (1998).

[9] S. Butorin, D. C. Mancini, J. H. Guo, N. Wassdahl, J. Nordgren, M. Nakazawa, S. Tanaka, T. Uozomi, A. Kotani, Y. Ma, K. E. Myano, B. A. Karlin, and D. K. Suth, Phys. Rev. Lett. **77**, 574 (1996).

[10] M. O. Krause, T. A. Carlson, and A. Fahlman, Phys. Rev. A **30**, 1316 (1984).

[11] A. Kay, E. Arenholz, B. S. Mun, F. J. Garcia de Abajo, C. S. Fadley, R. Denecke, Z. Hussain, and M. A. Van Hove, Science **281**, 679 (1998).

[12] F. J. Garcia de Abajo, C. S. Fadley, and M. A. Van Hove, Phys. Rev. Lett. **82**, 4126 (1999).

[13] E. Arenholz, A. W. Kay, C. S. Fadley, M. M. Grush, T. A. Callcott, D. L. Ederer, C. Heske, and Z. Hussain, Phys. Rev. B **61**, 7183 (2000).

[14] J. J. Jia, T. A. Callcott, J. Yurkas, A. W. Ellis, F. J. Himpsel, M. G. Samant, G. Stöhr, D. L. Ederer, J. A. Carlisle, E. A. Hudson, L. J. Terminello, D. K. Shuh, and R. C. C. Perera, Rev. Sci. Instrum. **66**, 1394 (1995).

[15] A. Moewes, S. Stadler, R. P. Winarski, M. M. Grush, T. A. Callcott, and D. L. Ederer, Phys. Rev. B **58**, R15 951 (1998).

[16] See, for example, S. Eisebitt, T. Böske, J.-E. Rubensson, and W. Eberhardt, Phys. Rev. B **47**, 14 103 (1993), or J. Jaklevic, J. A. Kirby, M. P. Klein, A. S. Robertson, G. S. Brown, and P. Eisenberger, Solid State Commun. **23**, 679 (1977).

[17] B. L. Henke, E. M. Gullikson, and J. C. Davis, At. Data Nucl. Data Tables **54**, 181 (1993).

[18] S. Büttner, A. Moewes, I. Storjohann, J. Voss, and C. Kunz, Annual Report No. HASYLAB/DESY, 1991 (unpublished).

[19] A. Kikas, E. Nommiste, R. Ruus, A. Saar, and I. Martinson, Solid State Commun. **115**, 275 (2000).