Physica Scripta

INCLUSIVE PUBLISHING TRUSTED SCIENCE

[K+L] double-electron transition in Fe

To cite this article: N Shigeoka *et al* 2005 *Phys. Scr.* **2005** 1084

View the article online for updates and enhancements.

You may also like

- Measurement of the O2O3O4 and O3O4O5 super Coster–Kronig rates in tungsten via asymmetric diffraction spectrometry
  John Seely, Jack L Glover, Lawrence Hudson et al.
- Characterization of the titanium K spectral profile
  C T Chantler, L F Smale, J A Kimpton et al.
- MODELING THE OXYGEN K ABSORPTION IN THE INTERSTELLAR MEDIUM: AN *XMM-NEWTON* VIEW OF Sco X-1
  J. García, J. M. Ramírez, T. R. Kallman et al.

This content was downloaded from IP address 18.116.81.199 on 18/05/2024 at 04:38

Physica Scripta. Vol. T115, 1084–1087, 2005

[K+L] Double-Electron Transition in Fe

N. Shigeoka[1,*], H. Oohashi[1], T. Tochio[1], Y. Ito[1], T. Mukoyama[2], A. M. Vlaicu[3], H. Yoshikawa[3] and S. Fukushima[3]

[1]Institute for Chemical Research, Kyoto University, Uji, Kyoto, 611-0011 Japan
[2]Kansai Gaidai University, 16-1 Nakamiyahigashino, Hirakata, Osaka 573-1001 Japan
[3]National Institute for Material Science, SPring-8, Mikazuki, Hyogo, 679-5198, Japan

Received June 26, 2003; accepted November 4, 2003

PACS number: 32.30.Rj, 32.80.Fb

Abstract

Fe K$\alpha_{3,4}$ satellite spectra are investigated using a Johann-type spectrometer at the BL15XU undulator beam line, SPring-8. Intensity of the K$\alpha_{3,4}$ satellite relative to the Kα_1 emission line is found to increase asymptotically with excitation energy up to 9000 eV, and almost saturates at around 9500 eV. Satellite threshold energy is found to be 7882 eV $\pm$ 14 eV. This corresponds to the ionization energy of Fe 1s + 2p*, where * indicates that the value is from the $Z+1$ approximation. The growth of satellite intensity with the excitation energy suggests that the 2p spectator holes are mainly created by shake-off in Fe, as suggested by Fritsch *et al.* [Phys. Rev. A **57**, 1686 (1998)] in a previous work on copper.

1. Introduction

Most studies into the contributions of shake processes in solids, vapors, etc. on X-ray absorption for elucidating electron correlations in atoms have been carried out by an Italian group, a Slovenian group, and a Japanese group *etc.* [1–10]. Extended shake-off saturation profiles are of special interest in X-ray absorption spectroscopy, as well as sharp multielectron photoexcitation features caused by resonance and shake-up [4, 5, 7, 10].

X-ray absorption of 3d transition metals has been examined in the K + L double photoabsorption energy region. However, no significant features attributable to multiple photoexcitation have been found in the spectra, and thus K + L edges in 3d elements have not been confirmed [3, 11]. This result could be explained by theoretical predictions of lower shake-up probabilities for K + L transitions [11], which predict that the transition edges observed in X-ray absorption spectra are due entirely to the shake-up process. That is, resonance and shake-up probabilities in the K + L transition of 3d elements are typically lower than detection accuracy so that pure long-range shake-off profiles in XAFS oscillations are difficult to obtain.

With the advent of third generation synchrotron radiation, experiments can be conducted on the threshold behavior of satellites, including the excitation dynamics of atoms. In particular, X-ray emission spectroscopy is suitable for studying satellites for electron correlation. The first detailed photoexcitation measurements were performed by Deslattes *et al.* [12], who examined multielectron vacancies in atomic argon using a combination of both emission and absorption spectroscopy. Deutsch and co-workers [13, 14] found pure shake-off behavior in the copper Kα X-ray satellite complex, and Sternemann *et al.* [15] measured the valence fluorescence satellite KM-N$_{2,3}$M transition of a solid germanium target. More recently Raboud *et al.* [16] measured the KL X-ray emission of argon induced by impact with monoenergetic photons to investigate the K + L double excitation from threshold to saturation.

The contributions of the 2s and 2p spectator transitions in 3d transition metals have only been investigated in copper. As investigation of lower Z 3d metals is needed to further understand multielectron excitation processes, spectator transitions in iron are investigated and presented.

2. Experiment

Measurements were carried out at the BL15XU undulator beam line, SPring-8, using a Johann-type spectrometer. A Si(111) double-crystal monochromator was used to generate a tuned X-ray excitation source, which has a bandpass of $\delta E/E \sim 10^{-4}$ and flux of over 10^{12}. A Johann geometry fluorescence spectrometer consisting of a 1.5-m-diameter Rowland circle on a horizontal plane and a curved Si(400) crystal was used to resolve fluorescence spectra. The spectrometer had a scanning range of 67° to 95°, and was evacuated to $\sim 10^{-3}$ torr using a scroll pump. A 20-μm-thick pure Fe foil was used as the sample. A NaI(Tl) scintillation counter was used to correct the signal and a N$_2$-gas-filled ionization chamber was used to monitor incident X-ray intensity in front of the target.

Two types of scan were used to investigate the excitation energy dependence of Fe K$\alpha_{3,4}$ spectra. First, the spectrometer was fixed in the Fe K$\alpha_{3,4}$ position ($2\theta \sim 91°$) and incident X-ray energy was scanned. X-rays were incident on the target at 75° to minimize the influence of fluctuations in incident beam spot position during the energy scan. From the first scan, a rough estimate of the K$\alpha_{3,4}$ satellite energy threshold was obtained, and energy values for the angle scan were determined. Several spectrometer angle scans were then conducted around $2\theta \sim 91°$, with excitation energy varied from 7850 eV to 10000 eV to trace variations in satellite spectra with excitation energy. During the angle scan, the incident angle of X-rays on the target was set to 45° to maximize fluorescence intensity at the detector.

3. Results and discussion

Results of the first scan around the threshold energy are shown in Figs. 1 and 2. The intensity of emissions at the Fe K$\alpha_{3,4}$ satellite complex energy can be seen to gradually increase as the excitation energy increases from around 8000 eV, and almost saturates at around 9500 eV, as shown in Fig. 1. Two lines are drawn in Fig. 2 to highlight the threshold of the satellites. Threshold values obtained from the $Z+1$ approximation are shown in the inset [17]. Values of [1s2p] ionization threshold energy are in agreement with the experimental results. Calculations of shake-up and shake-off probabilities in K + L double electron transitions were performed in a manner similar to Mukoyama and Ito [18] using the Dirac-Fock-Slater method [19], with results listed in Table I.

*Email address: yosi@elec.kuicr.kyoto-u.ac.jp

 © *Physica Scripta 2005*

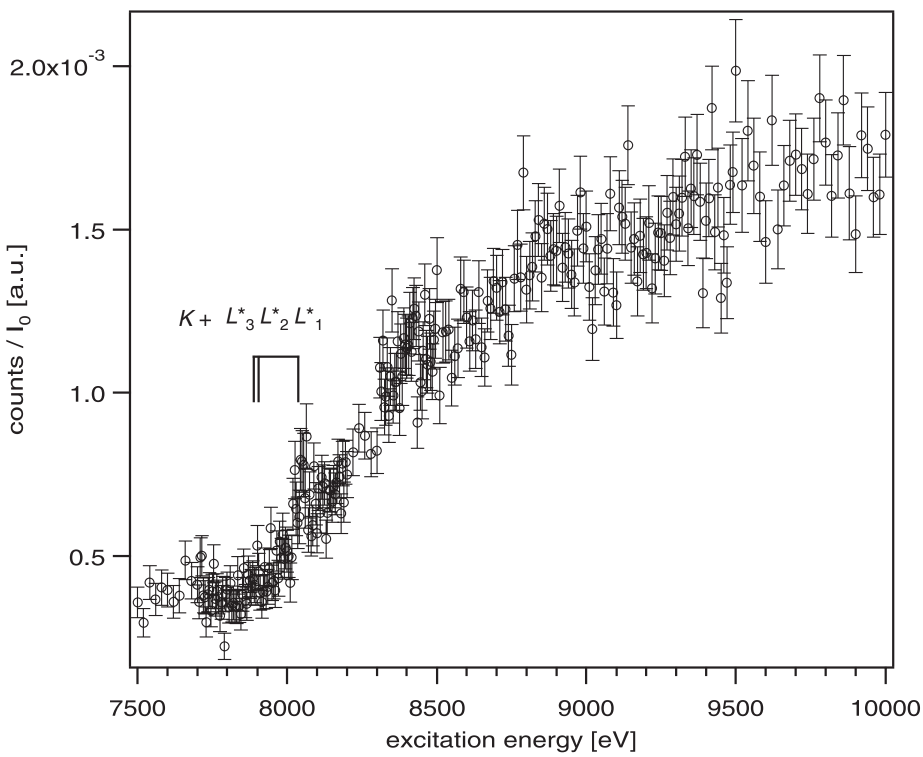

Fig. 1. Dependence of X-ray fluorescence emission intensity on excitation energy. Spectrometer 2θ was fixed at a position corresponding to the Fe $K\alpha_{3,4}$ emission. Excitation energy was scanned from 7500 eV to 10000 eV.

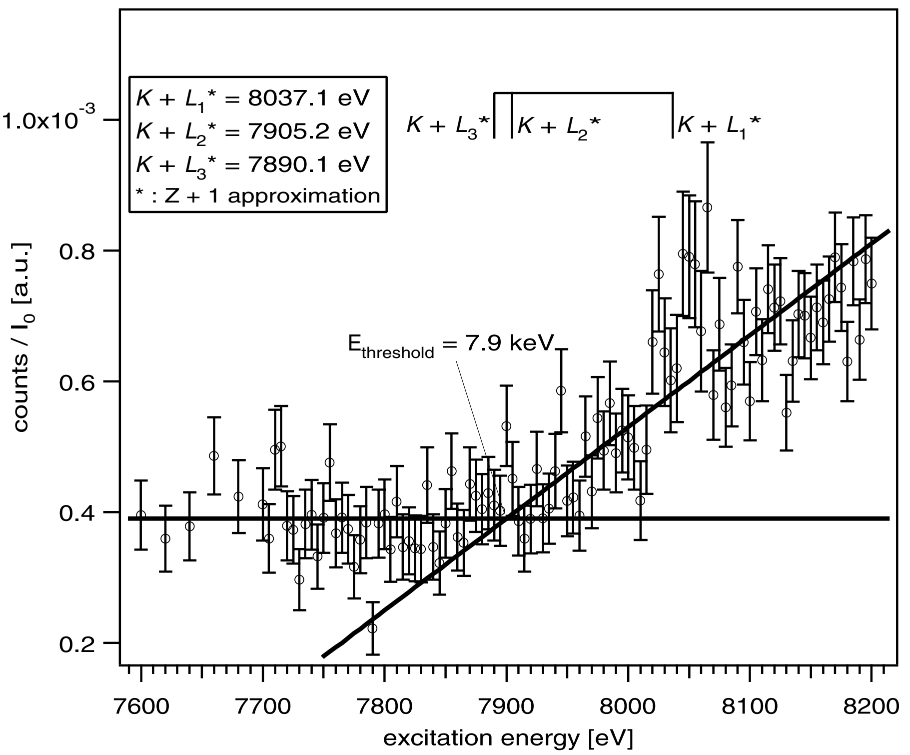

Fig. 2. Detailed plot of the data shown in Fig. 1 at around 7900 eV. Two lines have been drawn to highlight the threshold energy of satellite emissions. Values in the inset show the double hole creation threshold energies obtained by $Z + 1$ approximation. * indicate L sub-shell ionization energies in cobalt.

Moreover, a small intensity peak was clearly observed around the [1s2s] ionization threshold energy, possibly due to the appearance of a 2s hole. It is plausible that this peak is attributed to a resonance.

The observation of emissions influenced by 2s spectator holes is difficult compared to 2p holes because 2s spectator holes disappear faster than 2p holes through strong 2s2p Coster-Kronig transitions. Therefore contributions from [1s2s] shake processes may be observed as a part of satellite emissions with 2p spectator holes. If a 2s spectator hole is created and left around the small intensity peak in Fig. 2, the shape of the satellite complex may change due to the spectator hole itself. However, no clear evidence

Table I. *Probabilities of shake-up and shake-off involving L shells accompanied by K shell ionization in Fe using Dirac-Fock-Slater calculations. The $n = l$ column ($4 \le l \le 10$) shows the probability of shake-up to each $n = l$ shell.*

	Initial shells		
Destinations	L_1	L_2	L_3
$n = 4$		6.720×10^{-5}	1.323×10^{-4}
$n = 5$	1.300×10^{-5}	1.829×10^{-5}	3.645×10^{-5}
$n = 6$	4.990×10^{-6}	7.745×10^{-6}	1.549×10^{-5}
$n = 7$	2.448×10^{-6}	4.014×10^{-6}	8.040×10^{-6}
$n = 8$	1.382×10^{-6}	2.350×10^{-6}	4.711×10^{-6}
$n = 9$	8.567×10^{-7}	1.494×10^{-6}	2.998×10^{-6}
$n = 10$	5.675×10^{-7}	1.009×10^{-6}	2.025×10^{-6}
total shake-up	2.324×10^{-5}	1.021×10^{-4}	2.020×10^{-4}
shake-off	1.225×10^{-3}	1.975×10^{-3}	3.909×10^{-3}
total	1.248×10^{-3}	2.077×10^{-3}	4.111×10^{-3}

of contributions from 2s spectator holes could be confirmed within the accuracy of our experimental data.

Integrated intensity of the K$\alpha_{3,4}$ satellite complex is shown in Fig. 3 relative to the total K$\alpha_{1,2,3,4}$ emissions. Four reference data are also shown for comparison. The relative intensity of satellite complex can be seen to increase from 7900 eV and almost saturate at around 9500 eV. The data indicated by diamonds are experimental results from a conventional Fe X-ray tube measured using the same spectrometer as in the present work and an X-ray tube excitation voltage of 30 kV. The data indicated by triangles were measured using a double-crystal spectrometer. The target was pure Fe metal and a Rh X-ray tube with an excitation voltage of 40 kV was used. These values are in good agreement with the present 10000 eV experimental results, in which the satellites are almost fully developed. Data indicated by circles are calculated values of [1s2p] shake-off probability during K-shell ionization using the sudden approximation [20], and the circle with cross indicates the sum of calculated probabilities of [1s2s] and [1s2p] shake-off. The theoretical values, especially the latter, are in good agreement with the experimental results at an excitation energy of 10000 eV.

A small intensity peak is observed at an excitation energy of 8040 eV in Fig. 3 as well as in Fig. 2. This may be due to [1s2s] double electron excitation.

The solid line is the result of fitting the Thomas model [21] to the experimental data. In this model, the probability of creating a spectator hole via shake-off two-step-one (knockout of a second electron by the departing photoelectron) process is given by

$$P_{Thomas}(E_{ex}) = P_\infty \exp\left(\frac{-mr^2E_s^2}{2\hbar^2E_{ex}}\right),$$

where P_∞ is the probability at saturation, m is the mass of an electron, r is the distance covered by the photoelectron during the excitation process, and E_{ex} is the energy which is needed to excite a second electron. Replacing m and $\hbar$ with numerical values gives

$$P_{Thomas}(E) = P_\infty \exp\left(-\frac{r^2E_s^2}{15.32(E - E_{threshold})}\right).$$

During the fitting, E_s was fixed at 783.1 eV, P_∞ was fixed at 0.738% and other parameters were left free. The fixed E_s value was calculated from the weighted average of $L_{2,3}$ sub-shell binding energies of cobalt, obtained from the $Z + 1$ approximation. P_∞ was taken from the experimental value of the Fe X-ray tube (diamond in Fig. 3) that was measured using the same spectrometer as that in this work, but with an

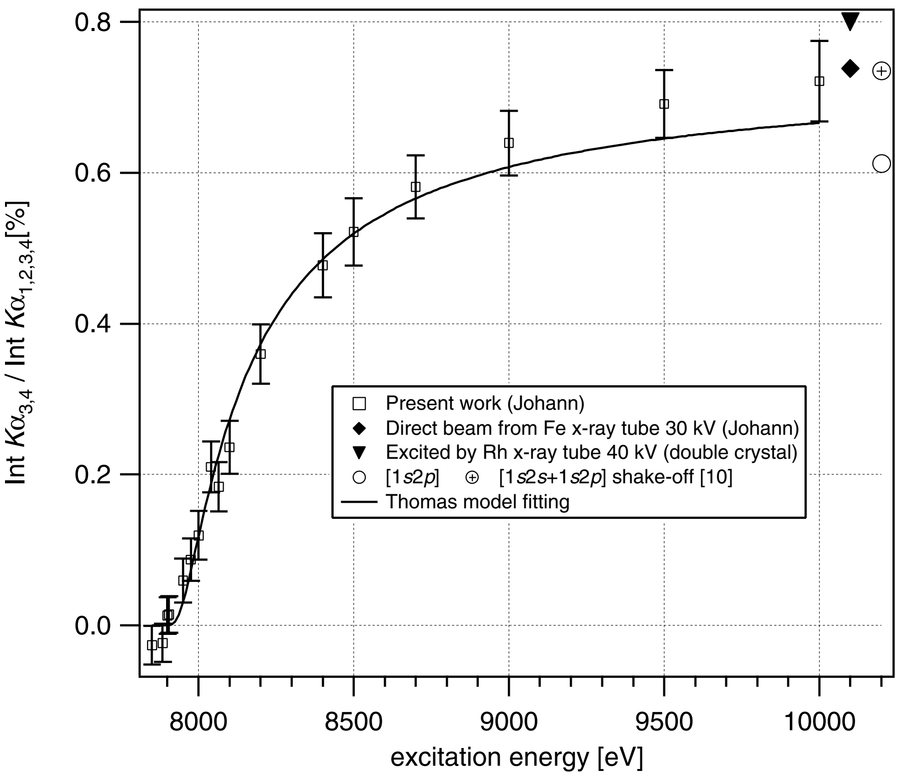

Fig. 3. Integrated intensity of K$\alpha_{3,4}$ satellite complex relative to total K$\alpha_{1,2,3,4}$ emissions. Squares with error bars show experimental data from the present work. Triangle, diamond, circle and circle with cross indicate experimental and theoretical reference values, as given by the legend. The solid line shows the results fitting to the Thomas model.

 © Physica Scripta 2005

excitation voltage of 30 kV at which the satellite is expected to be saturated. Results of the fitting were: $r = 0.074\,\text{Å} \pm 0.003\,\text{Å}$ and $E_{threshold} = 7881.6\,\text{eV} \pm 14.2\,\text{eV}$. The threshold energy of these fitting results is in good agreement with the [1s2p] excitation threshold energy from the $Z + 1$ approximation. The origin of the Fe K$\alpha_{3,4}$ satellites may be 2p spectator holes created by [1s2p] shake-off.

Less agreement between the fitting results and experimental values of excitation probability occurs for $E > 9000\,\text{eV}$, with the fitting function dropping below the experimental values. This may suggest that contribution of 2p spectator holes created by combination of matured [1s2s] shake-off and 2s2p Coster-Kronig transitions.

A shake-off process seems to dominate 2p spectator hole creation processes because the integrated intensity of satellite complex exhibits monotonic increase. The theoretical values listed in Table I also suggest that 2p vacancies in L shells are mainly created by the shake-off process.

4. Conclusion

The experimental evolution of Fe K$\alpha_{3,4}$ satellite complex from threshold to saturation was presented. The threshold energy of satellite complex was found to be around 7890 eV, matching the [1s2p] ionization threshold energy given by the $Z + 1$ approximation. The origin of Fe K$\alpha_{3,4}$ satellites seems to be spectator holes in the 2p levels (L_2 or L_3 shell).

The integrated intensity of Fe K$\alpha_{3,4}$ satellite complex exhibited a simple increase from threshold, indicating that a shake-off process is the origin of 2p spectator holes.

A small intensity peak was observed at around 8040 eV, corresponding to $K + L_1$ ionization threshold energy. The shape of this peak did not match shake-off or shake-up, but appeared to be a sharp resonance. The 2s hole also seems to appear around the same energy, but no clear change in the satellite was observed within the measurement accuracy. Strong 2s2p Coster-Kronig transitions may fill 2s holes quickly, with contributions from [1s2s] shake-off observed as satellite emissions with 2p spectator holes.

The conclusion is supported by the good agreement between the relative intensities at an excitation energy of 10000 eV and theoretical [1s2s + 1s2p] shake-off probabilities.

The experimental data in the saturated region agree well with theoretical values from the sudden approximation [20], but there are few models that can reproduce the evolution of this kind of shake-off satellite. The Thomas model of shake-off probabilities [21] agrees to some extent with our experimental data, and also with copper [13, 14] and argon [16] data, but the model still has room for improvement [14]. Therefore, a new model that describes the evolution of shake-off probability on a solid theoretical grounding is required in this field of investigation.

Further experimental work is also needed to push theoretical developments. Copper, argon and iron have now been measured, with further experiments on other 3d transition elements, rare gases and higher-Z elements needed to allow more detailed discussion in this field.

Acknowledgements

One of the authors (N. Shigeoka) would like to express his thanks to T. Shoji at the X-ray research laboratory, Rigaku Co., Takatsuki, Osaka for the preparation of curved analyzing crystals. This work was conducted at SPring-8 with the approval of the Independent Administrative Institution National Institute for Material Science as a Nanotechnology Support Project of the Ministry of Education, Culture, Sports, Science and Technology. (Proposal Nos. C02BL15XU-2009N & 2002B0438-NX-np/BL15XU).

References

1. Dángelo, P., Di Cicco, A., Filipponi, A. and Pavel, N. V., Phys. Rev. A **47**, 2055 (1993).
2. Filipponi, A. and Di Cicco, A., Phys. Rev. A **52**, 1072 (1995).
3. Kodre, A., *et al.*, Phys. Rev. A **45**, 4682 (1992).
4. Gomilšek, J., Kodre, A., Arčon, I., Loireau-Lozac'h, A. M. and Bénazeth, S., Phys. Rev. A **59**, 3078 (1999).
5. Gomilšek, J., Kodre, A., Arčon, I. and Preseren, R., Phys. Rev. A **64**, 022508 (2001).
6. Ito, Y., *et al.*, Phys. Rev. A **46**, 6083 (1992).
7. Ito, Y., *et al.*, Phys. Rev. A **51**, 303 (1995).
8. Mukoyama, T. and Ito, Y., Nucl. Instrum. Meth. Phys. Res. B **87**, 26 (1994).
9. Deutsch, M. and Hart, M., Phys. Rev. Lett. **57**, 1566 (1986).
10. Schaphorst, S. J., *et al.*, Phys. Rev. A **47**, 1953 (1993).
11. Ito, Y., *et al.*, Jpn. J. Appl. Phys. **32**, Suppl. 32 (1993).
12. Deslattes, R. D., LaVilla, R. E., Cowan, P. L. and Henins, A., Phys. Rev. A **27**, 923 (1983).
13. Deutsch, M., Gang, O., Hämäläinen, K. and Kao, C. C., Phys. Rev. Lett. **76**, 2424 (1996).
14. Fritsch, M., *et al.*, Phys. Rev. A **57**, 1686 (1998).
15. Sternemann, C., Kaprolat, A., Krisch, M. H. and Schülke, W., Phys. Rev. A **61**, 020501(R) (2000).
16. Reboud, P.-A., *et al.*, Phys. Rev. A **65**, 062503 (2002).
17. Bearden, J. and Burr, A., Rev. Mod. Phys. **39**, 125 (1967).
18. Mukoyama, T. and Ito, Y., Bull. Inst. Chem. Res., Kyoto Univ. **71**, 398 (1993).
19. Liberman, D. A., Cromer, D. T. and Waber, J. T., Comput. Phys. Commun. **2**, 107 (1971).
20. Mukoyama, T. and Taniguchi, K., Phys. Rev. A **36**, 693 (1987).
21. Thomas, T. D., Phys. Rev. Lett. **52**, 417 (1984).