UCRL-100904
PREPRINT

L-Shell Photoabsorption Spectroscopy
for Solid Metals: Li, V, Cr, Fe, Ni, Cu

Nancy Kerr Del Grande

This paper was prepared for submittal to
Ninth International Conference on
Vacuum Ultraviolet Radiation Physics
Honolulu, HI
July 17-21, 1989

September 13, 1989

Lawrence
Livermore
National
Laboratory

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

L SHELL PHOTOABSORPTION SPECTROSCOPY FOR SOLID METALS: Ti, V, Cr, Fe, Ni, Cu

Nancy Kerr Del Grande

UCRL--100904

Lawrence Livermore National Laboratory
P.O. Box 808, Livermore, California 94550

DE90 001510

Abstract

Synchrotron radiation measurements of near-threshold and broad-range (400-1500 eV) absolute photoabsorption cross sections were made for five transition metals with $\pm 10\%$ overall uncertainties. Fine structure details of 2p-3d autoionizing resonances are shown with better than 1.0 eV resolution for solid metals: Ti, V, Cr, Fe, Ni, and Cu. Fine structure similar to what we measured can be produced using a multi-configuration Dirac Fock (MCDF) model if a statistical distribution is assumed for the initial atomic states. Calculations were performed in intermediate coupling with configuration interactions by Mau H. Chen. The results are compared with other experimental work and theoretical methodologies.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

MASTER

tb

1. Introduction

A perusal of current photoabsorption cross sections which bracket the 2p thresholds of 3d transition metals Ca-Cu requires more and better measurements to refine theoretical methodologies [1-4]. Over the energy range 400-1500 eV half of these metals have been measured at only two or less photon energies [2]. Where there is overlapping data, disagreements exist. For example, discrepancies are nearly 50% for Ti below the L_3 absorption edge energy and a factor of two for Cu above the L_1 absorption edge energy. Also, at the higher energies above the 2p thresholds the published data for Ti, Cr and Ni are consistently about 60% lower than predictions of theory which is based on a relativistic version of the Hartree-Slater model [2,5].

This paper is part of a systematic effort to improve this situation. It follows our previous work on the measurements of cross sections for Fe and Ni between 1 and 2 keV and at higher energies with overall uncertainties of $\pm 3\%$ obtained using conventional laboratory x-ray sources [6]. Here we report measurements of absolute photoabsorption cross sections for the 3d transition metals Ti, Cr, Fe, Ni and Cu at 400-1500 eV with overall uncertainties of $\pm 10\%$ by using synchrotron radiation (SR). The results are compared with various theoretical calculations.

2. Experimental Procedure

We have already reported the details of synchrotron radiation measurement procedures for determining near-threshold and broad-range absolute photoabsorption cross sections at (20 eV to 3 keV) [7-11] including preliminary results for carbon and uranium with 10% overall uncertainties and better than 0.2% energy resolution [7]. Special techniques were developed to obtain reliable SR sub-keV cross section measurements in transmission [8,9]. They will be summarized in this paper. Examples were given showing the near-threshold resonance behavior for beryllium, carbon, nickel and uranium [8,9].

The special techniques used to obtain reliable cross section data include: (1) filtration to remove SR source contaminants from high order radiation and specularly reflected light; (2) characterization of the effective energy range and response of optical elements associated with detection of SR; (3) fabrication of free-standing carbon-metal multi-layered 100-4000 nm thick targets with improved strength, stability and protection from exposure to the atmosphere [10]; and (4) determination with 5 or 10 percent accuracy of the composition and separate areal densities of carbon and metal layers for the carbon-metal multilayer targets using a combination of MeV ion-beam backscattering techniques, ion-induced x-ray emission and direct measurements of target and

simultaneously prepared carbon-only component weights and areas [11].

Samples for the present measurements were prepared onto carbon films in a magnetron sputter deposition system with a base pressure of 2×10^{-7} Torr and a shutter arrangement for simultaneous depositions of carbon-only and carbon-metal foils. These samples were floated onto preweighed aluminum foil washers which were subsequently reweighed and mounted on target holders. The metal areal densities were determined from the average weight per unit area values derived from direct measurements and Rutherford backscattering measurements which differed at most by 5 or 10 percent.

Our data reported herein include absolute cross section measurements for Ti, Cr, Fe, Ni and Cu and the relative near-threshold behavior for V in addition to that of Ti, Cr, Fe, Ni and Cu. These data were taken using a spherical grating monochromator, various prefilters and a gold photo diode detector at the Stanford Synchrotron Radiation Laboratory (SSRL) Beam Line VIII-2 (BL-8 SSRL). It was necessary to normalize these data to earlier measurements taken at overlapping energy intervals with several well-characterized targets where the determination of the target areal density (mass per unit area) was known to better than $\pm 10\%$. For Ti and Cr these earlier measurements were taken at Brookhaven using Beam Line U14A (BL-U14 NSLS) at the National Synchrotron Light Source [7]. For Ni and Cu these earlier measurements were

taken at the SSRL Beam Line III-4 (BL-3 SSRL) using two layered synthetic microstructure (LSM) "crystals" which extended the measurement range to 2 keV [12]. For Fe these earlier measurements were taken at energies between 1 and 2 keV using conventional laboratory sources. Comparisons of these Fe measurements above 1 keV with two theoretical methodologies [5,13] were made and reported [6]. Agreement between calculation and measurement was better than $\pm 5\%$.

We used two or more target thicknesses to obtain less than 2% statistical fluctuations for all of our cross section measurements. It was necessary to determine broad-range cross sections with thicker targets which had photon penetration depths one-third to three mean free paths thick at energies away from edges. It was also necessary to have thinner targets (by a factor of three or four) to resolve the close-in structure. Clearly it would be difficult to make absolute cross section measurements using only one target thickness at an edge where the resonance represents a factor of ten or more change in the mean free path thickness value.

3. Experimental Results

For the convenience of the readers and also for comparison with other data, in Figure 1a we show the 1989 update, extension and revision of the widely-used semi-empirical tables [3,4]. This revision includes some of our preliminary broad range data for Ti,

Cr, Ni and Cu which we show here respectively in Figure 1b, 1c, 1e and 1f.

The effect of oxide impurities in Figure 1c for chromium and Figure 1d for iron is apparent. Synchrotron radiation sources allow continuous coverage above and below the oxygen K absorption edge to correct for such effects. Such corrections were possible after we obtained broad band coverage above and below the oxygen K absorption edge at 543 eV. They were not available for our preliminary (uncorrected) chromium data shown in Figure 1a.

4. Discussion

The Figure 1 comparisons of theory with experiment show good agreement for most of the 3d transition metals below and at twice the energy of the ionization threshold. Calculations shown as dashed lines in 1a were made using the relativistic time dependent local density approximation (RTDLDA) model [13]. Calculations shown as long dashed lines in 1 b-f were based on the single particle Hartree Slater (HS) model. The HS model was used to extend the Lawrence Livermore Laboratory semi-empirical data base photoabsorption cross-sections to sub-keV energies [14].

Near threshold resonance structure is not apparent in Figure 1a since the energy spacings are not fine enough. Also, high resolution SF 3d transition metal photoabsorption measurements were not

available until now. The prominent 2p-3d autoionizing resonances shown in Figure 1b-e completely mask the often used L_3 and L_2 absorption edge "saw tooth" structure. This "saw tooth" structure is merely an approximation used for convenience in representing the photoabsorption data broad range behavior [14].

The 2p-3d autoionizing resonances probe directly the angular momentum content of unoccupied 3d electronic states. They are associated with bound-bound transitions which lead to non-radiative Auger rearrangement of inner shell electrons. Such processes are not included in the HS model calculations represented by long dashed lines in Figure 1. Thus, the factor of two to four differences between our measurements and HS theory are not surprising at energies within 25 eV to 40 eV above the respective L_3 absorption edges of solid metals Ti, Cr, Fe and Ni.

We note that extended x-ray absorption fine structure (EXAFS) is apparent between the L_2 and L_1 absorption edges and has a significant broadening effect at the L_1 edge energy for Ti, Cr, Fe, Ni and Cu. EXAFS is determined mostly by the local geometry to and number of atoms in adjacent shells.

5. Theoretical Methodologies

Discrepancies result when we compare the linearized augmented plane wave (APW) solid state calculations in Figure 2 [15] with our high resolution SR measurements of 2p-3d autoionizing resonances in Figure 3. There is a build up in the relative intensity of the 2p $3/2$ resonance compared to the 2p $1/2$ resonance at their respective L_3 and L_2 absorption edges. This build up occurs as the 3d shell becomes filled. There are eight, six, four, two and zero 3d vacancies respectively for Ti, Cr, Fe, Ni and Cu. The lighter, low atomic number metals with more 3d vacancies have relative L_3 to L_2 resonance intensities significantly less than the apparent two to one ratios shown in Figure 2. Copper which has no 3d vacancies has no 2p-3d autoionizing resonances. However, some (much smaller) 2p-4d autoionizing resonance structure is evident. Since the measured total cross sections have two major components (associated with bound-bound and bound-free transitions) calculations must be refined to determine the relative contributions of these two components before true comparisons can be made with the measured photoabsorption cross sections. Our observations were that within the experimental uncertainties, the oscillator strengths for the Ti relative to the Ni bound-bound transitions are about four to one. This is expected since Ti has eight vacancies, or four times as many vacancies as Ni, in its respective unfilled 3d subshells.

In Figure 4 we show the unpublished results of theoretical calculations of atoms for bound-bound transitions using the Multi-Configuration Dirac Fock (MCDHF) Model by Mau H. Chen [16]. This ab initio calculation was performed in intermediate coupling assuming a statistical distribution of initial states. The calculations were folded with a resolution function to simulate an experimental resolution of 0.3%. For the moment it is not clear why the assumption of a statistical distribution of initial states gives results in relative agreement with, the line shape of our measurements for solid Ti and Ni metals shown in Figure 5, whereas the common assumption of the ground state for atomic Ti and Ni does not agree with our measurements. This would imply that where comparisons can be made in Figures 3, 4 and 5 for Ti, V, Fe, and Ni, the near edge fine structure is basically atomic in nature. The assumption of a statistical distribution of initial states must account for some important property of the solid. Fusion of atomic and condensed matter theoretical methodologies appears to be warranted.

We show in Figure 6 and Figure 7 other experimental methods and density of state (DOS) calculations which address this general area of research [17,18]. The electron energy loss spectroscopy results in Figure 6 show structures quite similar to what we have measured using high resolution photoabsorption spectroscopy in Figure 3. Computational methods are described which treat the atomic Coulomb

and exchange interactions as well as the solid-state band-structure effects [18].

6. Summary and Conclusion

We have shown the potential of new and better absolute photoabsorption cross sections to prompt refinement and testing of theoretical methodologies. More and better photoabsorption data, a critical review of existing data and refinement of theoretical methodologies should go hand in hand with progress toward providing quantitative results for a better understanding of photoabsorption over the sub-keV energy region.

7. Acknowledgements

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405 - ENG - 48. The author is indebted for the recent detector improvements, SR beam characterizations and critical reviews to K. G. Tirsell with whom she has collaborated extensively in previous work [7,8,9] and without whom timely *progress toward improving SR photoabsorption measurements in transmission* would have been difficult. Also she gratefully acknowledges Mau H. Chen for providing the unpublished calculations and E.M. Gullikson for making available the revised semi-empirical tables of B. L. Henke and his collaborators.

References

1. Manson, S.T., "Photoabsorption and photoionization cross sections: an overview of the current state of knowledge," in X-Ray and VUV Interaction Data Bases, Calculations, and Measurements, Del Grande, N. K., Lee, P., Samson, J. A. R., and Smith, D. Y., Eds., Proc. SPIE 911 pp. 2-5, 1988. Private communication (1989).
2. Saloman, E. B., Hubbell, J. H., and Scofield, J. H., "X-ray attenuation cross sections for energies 100 eV to 100 keV and elements $Z = 1$ to $Z = 92$," Atomic Data and Nuclear Data Tables 38, pp. 1-145, 1988.
3. Henke, B. L., Lee, P., Tanaka, T. J., Shimabukuro, R. L., and Fujikawa, B. K., "Low energy x-ray interaction coefficients: photoabsorption scattering and reflection, $E = 100$ -2000 eV, $Z = 1$ -94," Atomic Data and Nuclear Data Tables 27, pp. 1-144, 1982.
4. Henke, B. L., Gullikson, E. M., Davis, J. C., Fryer, M., Oren, A., "Update of our 1982 Low Energy X-Ray Photoabsorption and Scattering Factor Tables," in X-Ray and VUV Interaction Data Bases, Calculations, and Measurements, Del Grande, N. K., Lee, P., Samson, J. A. R., and Smith, D. Y., Eds., Proc. SPIE 911 pp. 107-121, 1988.
5. Scofield, J. H., "Theoretical photoionization cross sections from 1 to 1500 keV," Lawrence Livermore National Laboratory Report No. UCRL-51326, 1973. Private communication (1989). Ref. No. 2 for 100 eV to 100 keV range.
6. Del Grande, N. K., "Measured 1 to 40 keV photoabsorption cross sections for Fe, Ni, Sn, Ta, Pt, Au, Pb, U," in X-ray Imaging II, Knight, L. V. and Bowen, D. K., Eds., Proc. SPIE 691, pp. 2-10, 1986.
7. Del Grande, N. K., Tirsell, K. G., Schneider, M. B., Garrett, R. F., Kneedler, E. M. and Manson, S. T. (1988) "Resonances in near-threshold x-ray photoabsorption of inner shells," J. Phys. (Paris) 48, C9, pp. 951-954, 1987.

8. Del Grande, N. K., Tirsell, K. G., "Program to obtain reliable photoabsorption cross sections," in X-ray and VUV Interaction Data Bases, Calculations, and Measurements, Del Grande, N. K., Lee, R., Samson, J. A. R., and Smith, D. Y., Eds., Proc. SPIE 911, pp. 6-10, 1988.
9. Tirsell, K. G. and Del Grande, N. K., "Considerations for the use of synchrotron radiation sources to measure sub-keV x-ray photoabsorption cross sections in transmission," in X-ray and VUV Interaction Data Bases, Calculations, and Measurements, Del Grande, N. K., Lee, R., Samson, J. A. R., and Smith, D. Y., Eds., Proc. SPIE 911, pp. 146-156, 1988.
10. Weed, J., "Preparation of multilayered x-ray photoabsorption targets," in X-ray and VUV Interaction Data Bases, Calculations, and Measurements, Del Grande, Lee, P., Samson, J. A. R., and Smith, D. Y., Eds., Proc. SPIE 911, pp. 166-168, 1988.
11. Musket, R. G., "Composition and thickness of multilayer foils using MeV ion beam techniques," in X-ray and VUV Interaction Data Bases, Calculations, and Measurements, Del Grande, Lee, P., Samson, J. A. R., and Smith, D. Y., Eds., Proc. SPIE 911, pp. 177-184, 1988.
12. Barbee, T. W., Jr., "Application of multilayered optics monochromators to cross section determinations: x-ray and VUV," in X-ray and VUV Interaction Data Bases, Calculations, and Measurements, Del Grande, Lee, P., Samson, J. A. R., and Smith, D. Y., Eds., Proc. SPIE 911, pp. 169-176, 1988. BL-3 SSRL data were taken in collaboration with T. W. Barbee, Jr. See also unpublished Lawrence Livermore Laboratory Report UCRL-52000-87-11, 12 p. 22 and 51, Nov.-Dec. 1987.
13. Doolen, G. and Liberman, D., Physica Scripta 36, 77 (1987).
14. Plechaty, E., Cullen, D. and Howerton, R., Lawrence Livermore Laboratory Report UCRL-50400, 6, Rev. 3, 1981.

15. Müller, J. E., Jepsen, O, and Wilkins, J. W., "X-ray absorption spectra: K-edges of 3d transition metals, L-edges of 3d and 4d metals, and M-edges of palladium," Solid State Communications, Vol. 42, No. 5, pp. 365-368, 1982.
16. Chen, M. H., "Relativistic Auger and x-ray emission rates of the $1s2l^n(2l')^m$ configurations of Be-like ions," Physical Review A, Vol. 31, No. 3, pp. 1449-1457, 1984 and private communication, 1989.
17. Fink, J., M., Th. Müller-Heinzerling, and Scheerer, B., Speier, W., Hillebrecht, F. U., Fuggle, J. C., Zaanen, J. and Sawatzky, G. A., "2p absorption spectra of the 3d elements," Physical Review B, Vol. 32, No. 8, pp. 4899-4904, 1985.
18. Zaanen, J., Sawatzky, G. A., Fink, J., Speier, W., Fuggle, J. C., "L_{2,3} absorption spectra of the lighter 3d transition metals," Physical Review B, Vol. 32, No. 8, pp. 4905-4913, 1985.

Figure Captions

- Figure 1. Photoabsorption cross-section in cm^2/g showing in (a) the 1989 LBL (Henke) revision of 1982 semi-empirical tables [3,4] where the solid line is a data fit and the dashed line is based on RTDLDA theory [13]. Measurement with 10% overall uncertainties are compared with the 1981 LLNL sub-keV theoretical data base [14] for Ti in (b), Cr in (c), Fe in (d), Ni in (e) and Cu in (f).
- Figure 2. Absorption spectra calculation using linearized augmented plane wave (APW) method (Müller et al. 1982) [15].
- Figure 3. Measured L edge autoionizing resonances for transition metals Ti, V, Cr, Fe, Ni and Cu.
- Figure 4. L edge autoionizing resonances from multi-configuration Dirac Fock calculation assuming a statistical distribution of initial states in intermediate coupling (Chen, 1984) [16]. Private communication (1989).
- Figure 5. L edge autoionizing resonances: a comparison of experiment with calculations (Chen, 1989 [16] and Müller et al., 1982 [15]). The experiment measures the effect of the bound-bound plus bound-free transitions whereas the MCDF theory calculates the bound-bound component.
- Figure 6. $L_{2,3}$ edges of the 3d metals Ca-Ni based on electron energy-loss spectroscopy (Fink et al., 1985) [17,18].
- Figure 7. Comparison of electron energy-loss spectroscopy with bremsstrahlung isochromat spectra (BIS), and density of state (DOS) calculations (Fink et al., 1985) [17,18]. The solid and dotted lines show the respective total and partial density of states.

Figure 1. Photoabsorption cross-section in cm^2/g showing in (a) the 1989 LBL (Henke) revision of 1982 semi-empirical tables [3,4] where the solid line is a data fit and the dashed line is based on RTDLDA theory [13]. Measurement with 10% overall uncertainties are compared with the 1981 LLNL sub-keV theoretical data base [14] for Ti in (b), Cr in (c), Fe in (d), Ni in (e) and Cu in (f).

Figure 2. Absorption spectra calculation using linearized augmented plane wave (APW) method (Müller et al. 1982) [15].

Figure 3. Measured L edge autoionizing resonances for transition metals Ti, V, Cr, Fe, Ni and Cu.

Figure 4. L edge autoionizing resonances from multi-configuration Dirac Fock calculation assuming a statistical distribution of initial states in intermediate coupling (Chen, 1984) [16]. Private communication (1989).

Figure 5. L edge autoionizing resonances: a comparison of experiment with calculations (Chen, 1989 [16] and Müller et al., 1982 [15]). The experiment measures the effect of the bound-bound plus bound-free transitions whereas the MCDF theory calculates the bound-bound component.

Figure 6. $L_{2,3}$ edges of the 3d metals Ca-Ni based on electron energy-loss spectroscopy (Fink et al., 1985) [17,18].

Figure 7. Comparison of electron energy-loss spectroscopy with bremsstrahlung isochromat spectra (BIS) and density of state (DOS) calculations (Fink et al., 1985) [17,18]. The solid and dotted lines show the respective total and partial density of states.