0

OFFICE OF NAVAL RESEARCH
GRANT N00014-94-I-0331

R & T Code 4133044
Robert Nowak

Technical Report No. 69 ([illegible])

Identification of Resonant, Two-Electron, and Inter-Atomic Features in K and L_{23} NEXAFS Spectra

by

D.E. Ramaker, H. Sambe, H. Qian and W.E. O'Grady

Prepared for Publication

in

Physics Scripta

George Washington University
Department of Chemistry
Washington, D.C.

September 1994

918

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
September 1994

3. REPORT TYPE AND DATES COVERED
Technical Sept'93-Oct'94

4. TITLE AND SUBTITLE
Identification of Resonant, Two-Electron, and Inter-Atomic Features in K and L_{23} NEXAFS Spectra.

5. FUNDING NUMBERS
Grant #:
N00014-94-I-0331
Robert Nowak, Prog Off
R & T: 4133044

6. AUTHOR(S)
D.E. Ramaker, H. Sambe, X. Qian and W.E. O'Grady

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Chemistry Department
George Washington University
Washington, D.C. 20052

8. PERFORMING ORGANIZATION REPORT NUMBER
Technical Report
#69

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE
Approved for public release and sale; distribution is unlimited

13. ABSTRACT *(Maximum 200 words)*

Experimental Cl K NEXAFS spectra for Cl^- hydrated in H_2O, and on passivated Al electrodes (below and above the pitting potential) have widely different spectral line shapes. Experimental K- and L_{23}-edge NEXAFS data for the alkali halides and rare gas solids are compared with FEFF6 calculated results to optimize code input parameters, test code validity, and identify many-body features in these model systems. Differences are shown to arise from many-body shake-up and charge-transfer excitations. Although relatively small in the model spectra, the latter interatomic excitations are believed to be primarily responsible for the different Cl^- line shapes on the passivated Al electrodes.

14. SUBJECT TERMS
NEXAFS, Shake Satellites, X-Ray Absorption, Alkali Halides
Rare Gases

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
Unlimited

Version July 11, 1994

Identification of Resonant, Two-electron, and Inter-atomic Features in K and L_{23} NEXAFS Spectra

D.E. Ramaker[a,b], H. Sambe[a], H. Qian[a]
and W.E. O'Grady[b]

[a]George Washington University, Wash. DC 20052,
[b]Naval Research Laboratory, Wash., DC. 20375.

Abstract

Experimental Cl K NEXAFS spectra for Cl^- hydrated in H_2O, and on passivated Al electrodes (below and above the pitting potential) have widely different spectral line shapes. Experimental K- and L_{23}-edge NEXAFS data for the alkali halides and rare gas solids are compared with FEFF6 calculated results to optimize code input parameters, test code validity, and identify many-body features in these model systems. Differences are shown to arise from many-body shake-up and charge-transfer excitations. Although relatively small in the model spectra, the latter interatomic excitations are believed to be primarily responsible for the different Cl^- line shapes on the passivated Al electrodes.

Keywords: NEXAFS, Chloride ion, Alkali halides, Rare gases, Many-body features

Corresponding Author
David E. Ramaker
Chemistry Department
George Washington University
Washington, DC 20052
Tel. 202-994-6934 FAX: 202-994-6934
E-mail: Ramaker@GWUVM.GWU.EDU

1. Introduction

Recent near edge X-ray absorption fine structure (NEXAFS) data have been used to observe the Cl^- edge on passivated Al surfaces exposed to chloride solution as a function of the electrode potential above and below the pitting potential [1]. These spectra reveal that different chemical states of the chlorine atoms are present as a function of the electrode potential. In an attempt to understand the spectra of this complex disordered system, we undertook a study of several related model solids; namely alkali halides and rare gases. In the ionic picture, the alkali and halide ions are isoelectronic with rare-gas atoms.

2. Alkali halide results

Calculations utilizing the curved wave multiple scattering model (FEFF6 code [2]) on alkali halides involving Li^+, Na^+, K^+, Rb^+, F^-, Cl^-, and Br^- for both the metal and halide K- and L_{23}-edges were performed. Since the L_{23} edge is composed of the sum of the L_2 and L_3 edges, we developed an iterative method,

$$\mu_{i+1,L3}(E) = \{\mu_{i,L3}(E) + \alpha\, [\mu_{exp}(E) - R_{23}*\mu_{i,L3}(E-\Delta E_{23})]\}/(1+\alpha), \qquad (1)$$

to separate the two, with the L_2/L_3 branching ratio, R_{23}, and energy separation ΔE_{23} as input parameters, and where α is a convergence control parameter, normally chosen to be unity. Often R_{23} can be determined using the first few peaks in the experimental spectrum since they are well isolated and ΔE_{23} can be obtained from XPS data. This iterative procedure is found to converge in 5 to 10 iterations, even for poor initial guesses of the L_3 (e.g., $\mu_{i=0,L3} = \mu_{exp}$).

Fig. 1 compares the L_3 and L_2 components obtained from the experimental data for KCL[3]. The Cl-L_3 is compared with the Cl-d projected partial density of states (PDOS) obtained using the augmented plane wave method [4], and with FEFF6 results. The E_1 and E_2 excitonic states are not reproduced in the FEFF6 results. Except for R_7 , all R_i resonant features are evident, thus suggesting little two-electron contributions if any.

We found the following general trends in FEFF6. For insulators with large band gaps such as those examined here, use of the ground state exchange correlation potential without a constant imaginary part best reproduces experimental data below 20 eV while above 30 eV the Hedin-Iundquist self-energy is better. The inclusion of the core-hole (i.e. Z+1 effect) improves results, and the "non-ionic" calculations are better than the "ionic" calculations.

3. Condensed rare gas results

The NEXAFS spectra of solid Ne, Ar, and Kr, were examined utilizing FEFF6 calculations and gas phase spectra [5]. Seven features in the experimental K-edge NEXAFS of solid Ne that are not reproduced by the FEFF6 calculations are found to be attributable to two-electron excitations. Five of them are the usual one-center excitations coming from $1s2p \rightarrow 3p3p$ and $1s2p \rightarrow 3s3p$ shakeup excitations. The remaining two are novel two-center excitations involving semi-localized resonant orbitals, $1s_a2p_b \rightarrow 3p_a\epsilon_ip_b$, where the subscripts a and b imply different atomic centers. Two-center excitations involving only bound orbitals, such as $1s_a2p_b \rightarrow 3p_a3p_b$, do not appear because of the smaller relaxation upon creation of the core hole by the localized 3p compared with that of the semi-localized ϵ_ip orbital.

4. Cl⁻/Al electrode results

Large pre-edge features visible in the Cl K-edge NEXAFS for Cl^-/passivated Al electrodes, which are not reproduced in the FEFF6 results, and also not present in results for NaCl, are attributed to two-center charge-transfer satellites. A Larson-Sawatzky model [6] is utilized to explain these satellites, which are particularly large at the Al electrode surface, and suggest the presence of Cl^o at the surface, vs Cl^- in the bulk of the passivation layer (or in NaCl); with Cl^- in larger quantities just below the pitting potential.

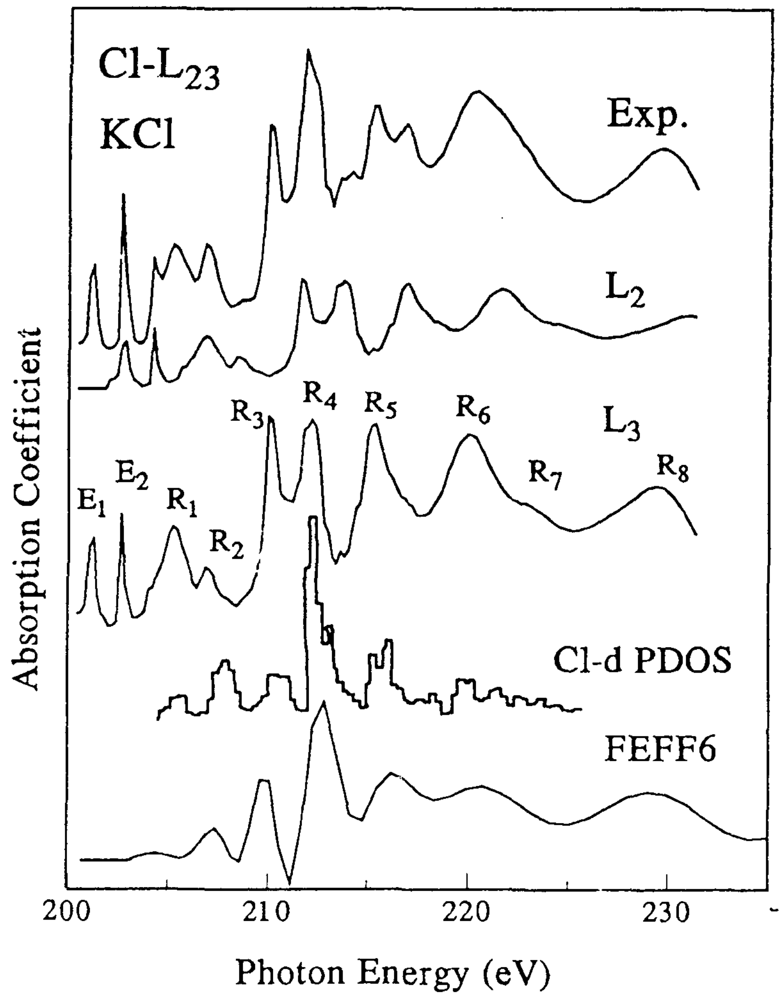
* Supported by the Office of Naval Research

References

1. W.E. O'Grady, E. McCafferty, P.M. Natishan, A. Russell, and D.E. Ramaker, K.I. Pandya, J. Electrochem. Soc., submitted.
2. J.J. Rehr, Jpn. J. Appl. Phys. 32, 8 (1993).
3. T. Sagawa et al, J. Phys. Soc. Jpn. 21, 2587 (1966).
4. I.I Gegusin et al, Phys. Stat. Sol. B109, 563 (1982).
5. H. Sambe, X. Qian, D.E. Ramaker, to be published.
6. S. Larsson, Chem. Phys. Lett. 40, 362 (1976); G. vanderLaan, et al, Phys. Rev. B23, 4369 (1981); B33, 4253 (1986).

Figure Caption

1. Decomposition of experimental [3] Cl K-edge NEXAFS (absorption) into the L_3 and L_2 components as described in the text (R_{23} = 2.0, ΔE_{23} = 1.6 eV), and comparison of the L_3 component with optimally aligned Cl-d projected PDOS [4] and with FEFF6 results (maximum MS scattering length 9.5 A^o with all paths included.i,e, criteria = 0, ground state exchange, and no mean free path corrections or Debye-Waller broadening). The core hole effect is included in the FEFF6 results, but not in the Cl-d PDOS. The Cl-s PDOS are ignored in both cases, and the transition matrix elements are not included in the Cl-d PDOS.


Cl-L_{23}
KCl
Exp.
L_2
L_3
E_1
E_2
R_1
R_2
R_3
R_4
R_5
R_6
R_7
R_8
Cl-d PDOS
FEFF6
Absorption Coefficient
200
210
220
230
Photon Energy (eV)