

Lawrence Berkeley National Laboratory

Recent Work

Title

Resonant Inelastic Scattering in Localized Solid State Systems by Soft X-Ray Fluorescence Spectroscopy

Permalink

<https://escholarship.org/uc/item/7dm6j1x1>

Journal

Journal of Electron Spectroscopy and Related Phenomena, 79

Authors

Perera, R.C.C.

Jia, J.J.

Callcott, T.A.

et al.

Publication Date

1995-08-07



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

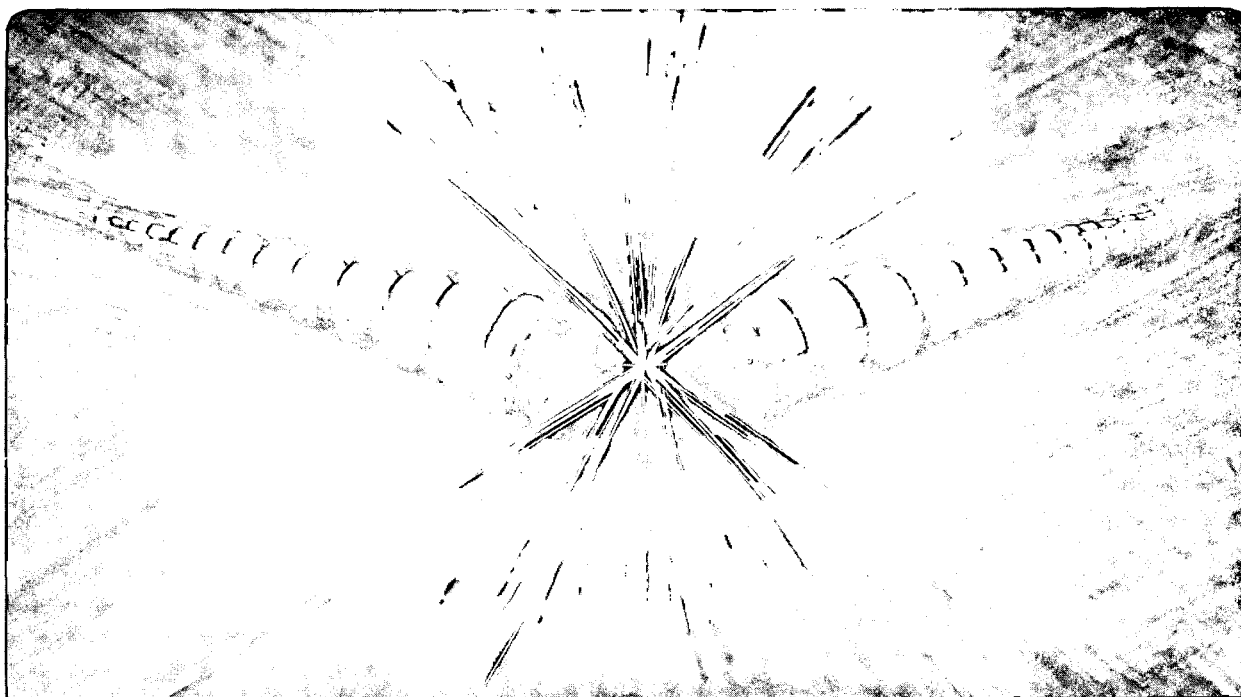
Accelerator & Fusion Research Division

To be presented at the Eleventh International Conference
on Vacuum Ultraviolet Radiation Physics, Tokyo, Japan,
August 27–September 1, 1995, and to be published in the
Proceedings

Resonant Inelastic Scattering in Localized Solid Systems by Soft X-ray Fluorescence Spectroscopy

R.C.C. Perera, J.J. Jia, T.A. Callcott, J.A. Carlisle,
L.T. Terminello, F.J. Himpsel, and D.L. Ederer

August 1995



REFERENCE COPY |
Does Not |
Circulate |
Bidg. 50 Library. |
Copy 1

LBL-37104

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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 product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of 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 any agency thereof or the Regents of the University of California.

**RESONANT INELASTIC SCATTERING IN LOCALIZED SOLID SYSTEMS
BY SOFT X-RAY FLUORESCENCE SPECTROSCOPY***

R.C.C. Perera
Advanced Light Source
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720, USA

J.J. Jia
University of Tennessee
Knoxville, Tennessee 37996

T.A. Callcott, J.A. Carlisle, L.T. Terminello
Lawrence Livermore National Laboratory
Livermore, CA 94551

F.J. Himpsel
IBM T.J. Watson Research Center
Yorktown Heights, NY 10598

D.L. Ederer
Tulane University
New Orleans, LA 70118

Paper submitted at The 11th International Conference
on Vacuum Ultraviolet Radiation Physics

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

LSSL- 2 6 02

Light Source Note:	
Author(s) Initials	WJ 8/7/95 Date
Group Leader's Initials	MP 8/10/95 Date

Resonant Inelastic Scattering in Localized Solid Systems by Soft X-ray Fluorescence Spectroscopy

R.C.C. Perera^a, J.J. Jia^b, T.A. Callcott^c, J.A. Carlisle^c, L.T. Terminello^c, F.J. Himpsel^d, and D.L. Ederer^e

^a Advanced Light Source, Lawrence Berkeley Laboratory, Berkeley, CA 94720

^b University of Tennessee, Knoxville, TN 37996

^c Lawrence Livermore National Laboratory, Livermore, CA 94551

^d IBM T.J. Watson Research Center, Yorktown Heights, NY 10598

^e Tulane University, New Orleans, LA 70118

An insertion device beamline, BL 8.0 at the ALS, utilizes the radiation from a 5.0 cm period undulator to cover the 100 - 1500 eV photon energy range. In a number of solid systems with localized conduction band states and excitonic states, by tuning the energy of the monochromatic x-rays near the core level absorption edges of cation atoms, a resonant inelastic scattering feature is observed. We have carried out careful studies in various systems. As an example, we present resonant X-ray inelastic scattering spectra from CaF₂, CaSi and CaSi₂ with distinctive localized empty 3d states, to give a general overview of resonant inelastic scattering observations in these systems. When a core electron is excited into a localized state, it stays there long enough eventually to recombine with the core hole, resulting in resonant elastic peaks. For the inelastic process, the energy loss observed indicates an electronic transition of the valence electron to the localized states in the conduction band accompanying the excitation. The valence band originating from the cation Ca is very narrow, yet the strong effects of inelastic scattering at the Ca 2p threshold are unambiguously observed.

1. INTRODUCTION

Soft x-ray fluorescence (SXF) emission is especially powerful because the shallow core levels have a natural width that is about a factor of 10 less than deeply bound levels¹. Thus, the valence-band spectrum is not unduly broadened by the width of the core level. Furthermore, because the fluorescence photons are not affected by electric and magnetic fields, insulating samples can be studied. Tunable synchrotron radiation has revived interests in x-ray fluorescence spectroscopy². The major barrier to widespread use of soft x-ray fluorescence spectroscopy, the low intensity of available sources, has been overcome with the advent of high brightness third generation synchrotron radiation (SR) sources like the Advanced Light Source (ALS) in Berkeley. Such SR sources are optimized for high spectral brightness in the soft x-ray and vacuum ultra-violet wavelengths.

Resonant emission phenomenon has been observed before, using electron beam excitation³ (by varying the electron beam voltage, C. Bonnelle and co-workers observed resonant features in the emission spectra of rare earth

metals and oxides, which coincide in energy with features in the absorption spectra), and laboratory x-ray sources⁴ resulting from the fortuitous location of the Ru L₃ absorption edge between the Pd L α ₁ and L α ₂ emission lines. The process involves the excitation of core electrons to a localized, empty state, and if the core hole lives long enough, the electron may recombine with the core hole and emit a photon subsequently. A resonant feature is observed only if a localized conduction band state (either an excitonic state or a discrete state hybridized with an extended state) exists. Thus selective excitations to the localized states provide an opportunity to study the localized states in a new angle⁵⁻⁷.

Soft x-ray fluorescence spectroscopy using photon excitation has a number of unique properties. Photons penetrate many atomic layers into the material. It is a true bulk probe of the electronic structure and is less affected by surface contamination than would occur if one used electron spectroscopy². Since a core hole of well-defined angular momentum is generated by a dipole transition in SXF, the method is site and angular momentum selective.

We have studied molecular gasses², buried interfaces⁶, and solid systems⁷ using resonant x-ray emission spectroscopy. As an example of resonant x-ray inelastic scattering, spectra from CaF₂, CaSi, and CaSi₂ with distinctive localized empty 3d states will be presented in this paper. Detailed analyses of these systems are presented elsewhere⁸.

2. EXPERIMENT

An insertion device beamline BL 8.0 at ALS is utilizing radiation from a 5.0 cm period undulator (U5.0) to deliver photons in the 70-1200 eV photon range⁹. The energy resolution, $E/\Delta E$ is better than 10^4 for the 100-200 eV region. Using refocussing optics, over 10^{12} ph/s in a 0.1% bandwidth can be delivered to about 100 μm spot size¹⁰.

One of the four end stations to utilize this undulator radiation is a high resolution soft x-ray emission (SXE) spectrometer, a grazing incidence, Rowland Circle instrument in which the diameter of the Rowland Circle can vary from 5 to 10 m. This spectrometer is designed to match the small phase-space attributes of the high spectral brightness of the beamline optical system. The fluorescence spectrometer has a fixed entrance slit, four spherical diffraction gratings, and a position-sensitive area detector. The gratings are interchangeable from outside the vacuum. The detector is a true photon counting device utilizing micro channel plates and a resistive anode readout. Emission spectra are measured by positioning the detector along the Rowland circle to intercept the spectrum of interest, and utilizing the area detector to record the entire spectrum simultaneously. Scanning is accomplished by a precision X-Y-z table on which the detector chamber is mounted. Both scanning and data acquisitions are automated through an IEEE-488 bus interfaced to a personal computer. Detailed description of the spectrometer is presented elsewhere¹¹. All measurements reported in this paper were made with an 100 mm entrance slit for the spectrometer, 1000 lines/mm, 10 meter radius grating. At the Ca L_{2,3} edges, the resolution of the spectrometer is approximately 1.0 eV. The energy resolution of the monochromator was set to be 0.3 eV during these measurements.

3. RESULTS AND DISCUSSIONS

In Fig. 1, the Ca L_{2,3} fluorescence spectra of CaF₂ for excitation energy varying from 346.0 to 353.3 eV are shown. The numbers labeling the curves are the excitation energies. Sharp elastic (recombination) peaks with varying intensity are obvious in these spectra for excitation energies

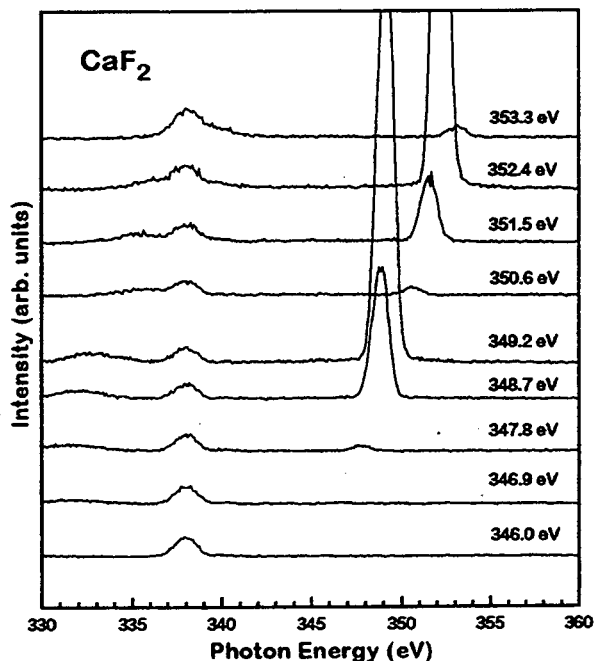


Fig. 1. The Ca L_{2,3} fluorescence spectra of CaF₂ excited by monochromatic photons of various energies near the Ca L edge. The numbers labeling the curves are the energies of the incident photons.

above 347.8 eV. It is apparent from figure 1 that the recombination peaks show strong resonance at both the L₃ (2p_{3/2}) and L₂ (2p_{1/2}) edges. The normal fluorescence (Ca L) is the narrow peak present at about 338 eV. This feature persists at all excitation energies and remains unchanged until the onset of the second Ca 2p-3d resonance, when the intensity of the high energy side increases to give it an asymmetric look. Further checking indicates that the asymmetry has significant contribution from the second order F K

fluorescence excited by the higher-order radiation that is inherent for a SGM monochromator.

The most interesting part of these spectra in figure 1 appears at about 333 eV region. At an excitation energy of 346 eV, the spectrum is clean without the presence of an elastic peak in this spectral region. With an increase of the excitation energy by just one eV, a broad spectral feature at about 333 eV is observed. The intensity of this spectral feature increased as the excitation subsequently being raised. It reaches its maximum value relative to the normal Ca L fluorescence, when the excitation energy is 349.2 eV, coinciding with the excitation of the largest elastic recombination peak.

The Ca L_{2,3} spectra of CaSi are shown in Fig. 2. Each spectrum is labeled with the photon energy used for its excitation. The normal fluorescence spectra, generated by the radiative recombination of Ca valence band states with the core hole, produce the spectral features that are centered near 343 eV and observed with off-resonance excitation. The energy loss features at about 335 eV region reaches its maximum value relative to the normal Ca L fluorescence, when

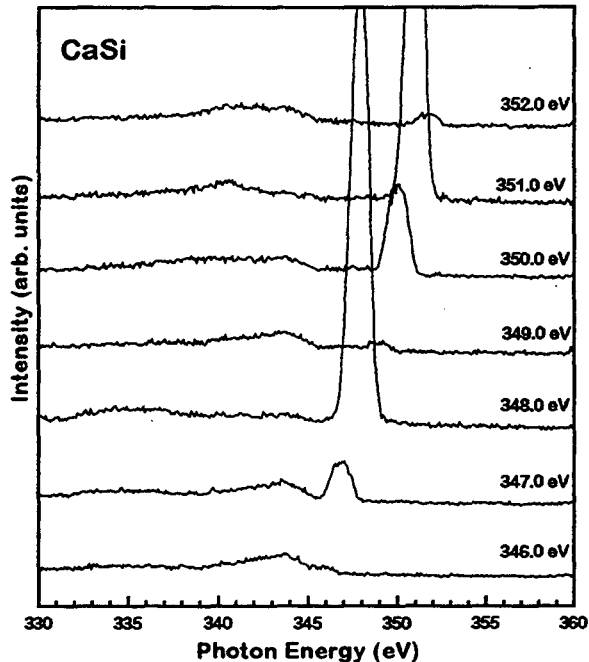


Fig. 2. The Ca L_{2,3} fluorescence spectra of CaSi with the excitation energies indicated.

the excitation energy is 348.0 eV, corresponding to the excitation of the maximum elastic recombination peak.

The Ca L_{2,3} fluorescence spectra of CaSi₂ are shown in Fig. 3. The normal Ca L fluorescence is observed at about 343 eV. Note that no prominent resonant inelastic peaks are resolved for CaSi₂, though a very weak displaced peak may be present centered at about 336 eV in the spectrum excited on the 348 eV resonance.

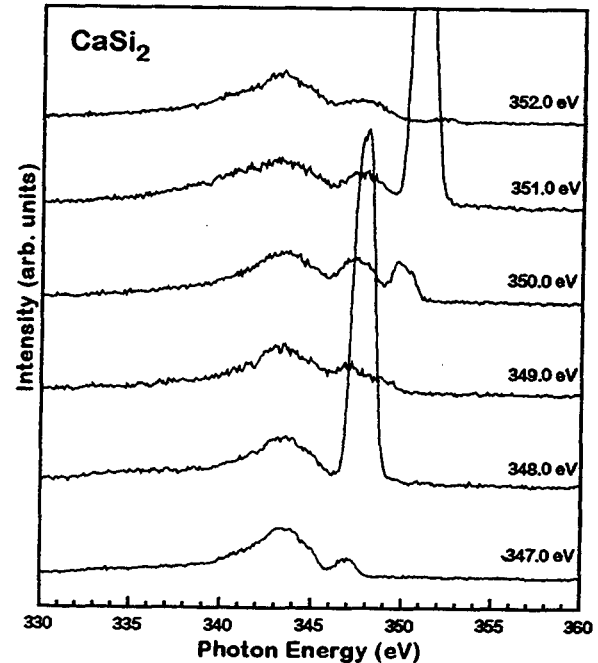


Fig. 3. The Ca L_{2,3} fluorescence spectra of CaSi₂ with the excitation energies indicated.

The resonant process can be understood as following: when monochromatic photons are tuned to excite Ca 2p core electrons into 3d states, the electrons stay in the d states due to its semi-discrete nature; and eventually they recombine with the core hole and give such large resonances. Extended conduction band states in de localized solid systems do not usually appear in fluorescence spectra, because electrons in these states quickly diffuse away from the core hole within the core lifetime before they radiate. The 3d states in Ca compounds are an intermediate case between atomic and well-extended states in

solids. The conduction band states are essentially a hybridization between Ca 3d states and extended s-p states. Thus, selective excitation of Ca 2p electrons using photons with energies corresponding to the Ca 2p-3d transition may also excite the core electron to the extended states, in which case the valence band electrons will annihilate the core hole, resulting in normal valence band fluorescence. The intensity ratio between the resonance from the 3d states and valence band fluorescence may provide an indication of the degree of hybridization between the Ca 3d states and the extended s-p conduction states. From Figs. 1, 2 & 3 the intensity ratios of the elastic peak to the valence band peaks for CaF₂ and CaSi are about 20, whereas the corresponding intensity ratio for CaSi₂ is about 7.

The appearance of inelastic scattering feature in Ca L spectra seems to be closely related to the localization factor of Ca 3d states. In a highly ionic compound like CaF₂, the valence band is derived largely from fluorine 2p atomic states. As a result, CaF₂ has very narrow valence band. The energy-loss feature is also present for the CaSi spectra, but not for CaSi₂. The Ca 3d states are more localized in CaSi than in CaSi₂, as evidenced by the ratio of recombination peak and main emission feature from the valence band. The extra silicon concentration in CaSi₂ obviously increased the interaction of the Ca d orbitals with de localized Si s- and p- orbitals. The resonant elastic recombination is quite strong in CaSi, as in CaF₂.

In conclusion, we have measured the Ca L_{2,3} fluorescence of CaF₂, CaSi and CaSi₂. The localized excitation of Ca 2p - 3d produces resonant recombination peaks. Prominent inelastic scattering features were observed below the valence emission. A coherent Raman-like inelastic scattering process is believed to be responsible for the observation of such features. The absence of the inelastic peak in CaSi₂ is consistent with both the reduced magnitudes of the elastic resonance and the stronger Ca d-, Si s- and p- bonding expected in the di-silicide.

4. ACKNOWLEDGMENTS

This work was supported by Office of Basic Energy Science of the Department of Energy under contract Nos. DE-AC03-76SF00098 and W-7405-Eng-48 and National Science Foundation Grant No. DMR-9017996 to the University of Tennessee.

5. REFERENCES

1. J. Nordgren, Proceedings of this conference and references therein.
2. D.L. Ederer, T.A. Callcott, and R.C.C. Perera, *Synchrotron Radiation News* 7 (1994) 29.
3. C. Bonnelle, *Advances in X-ray Spectroscopy*, eds. C. Bonnelle and C. Mande, p. 104 (1982).
4. J. Barth, R.C.C. Perera, R.E. LaVilla, and C. Nordling. Paper presented at the International Conference on X-ray and Inner Shell Processes, X84, Leipzig, Germany, August 20-24, 1984.
5. J.A. Carlisle, E.L. Shirley, E.A. Hudson, L.J. Terminello, T.A. Callcott, J.J. Jia, D.L. Ederer, R.C.C. Perera, and F.J. Himpsel, *Phys. Rev. Lett.* 74 (1995) 1234.
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 (1995) 34.
7. J.J. Jia, T.A. Callcott, A. Asfaw, J.A. Carlisle, L.J. Terminello, D.L. Ederer, F.J. Himpsel, and R.C.C. Perera, *Phys. Rev. B* 52 (1995).
8. J.J. Jia, T.A. Callcott, D.L. Ederer, J.A. Carlisle, L.J. Terminello, A. Asfaw, and R.C.C. Perera. To be published in *Phys. Rev. B*.
9. Insertion device participating research team at the ALS, a collaboration between IBM, LBNL, LLNL, University of Tennessee, and Tulane University.
10. R.C.C. Perera, *Nucl. Instrum. Methods A* 319 (1992) 277.
11. J.J. Jia, T.A. Callcott, J. Yurkas, A.W. Ellis, F.J. Himpsel, M.G. Samant, J. 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 (1995) 1394.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL AND ELECTRONIC
INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720