Lawrence Berkeley National Laboratory
Recent Work

Title
RESONANT RAMAN SCATTERING AS A SOURCE OF INCREASED BACKGROUND IN SYNCHROTRON INDUCED X-RAY FLUORESCENCE

Permalink
https://escholarship.org/uc/item/6tt8f7r8

Authors
Jaklevic, J.M.
Giauque, R.D.
Thompson, A.C.

Publication Date
1987-08-01
Resonant Raman Scattering as a Source of Increased Background in Synchrotron Induced X-Ray Fluorescence

J.M. Jaklevic, R.D. Giauque, and A.C. Thompson

August 1987
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.
ABSTRACT

Experiments studying the optimization of tunable monochromatic synchrotron radiation for x-ray fluorescence analysis have demonstrated the importance of resonant Raman x-ray scattering in establishing the minimum detectable limit for certain types of trace analysis. These analyses involve the measurement of elements with atomic numbers less than the predominant matrix elements in which the fluorescence of the matrix components is eliminated by selecting excitation energies immediately below major absorption edges. The cross section for Raman scattering from the matrix atoms can be resonantly enhanced resulting in a significant increase in continuum background below the fluorescence peaks of elements of interest. Significant increases in minimum detectable limits have been observed for gallium arsenide samples.

INTRODUCTION

The use of synchrotron radiation as an excitation source for x-ray fluorescence analysis has been discussed by many authors (1-3). A synchrotron source provides high incident flux, ease of collimation, and reduction of the scattered background as a result of beam polarization. For the case of tunable monochromatic radiation, it is also possible to optimize the sensitivity
for specific elements and to discriminate against other interfering elements by adjusting the energy of the incident beam with respect to major absorption edges of elements in the sample (4,5). Using these techniques, a minimum detectable limit of 100 ppb has been reported for highly focused beams incident on hydrocarbon matrices (6).

However, in the case of matrices of predominantly high atomic number material, the same optimization considerations do not necessarily apply. We describe an experiment in which the ability to select the excitation energy resulted in a substantial enhancement in continuum spectral background causing an unexpected degradation in the analytical sensitivity. The background is produced by resonant x-ray Raman scattering and is predominant for cases in which one selects an excitation energy immediately below a major absorption edge of the matrix material. This would be a normal approach for the analysis of elements which are of lower atomic number than those comprising the matrix since the fluorescence of the matrix could be eliminated by tuning to an energy below the absorption edge. Raman scattered background has previously been observed in the analysis of geological samples in which a variety of heavy element compounds were present in the matrix (7). However, for cases in which the matrix composition is primarily of an atomic number greater than that of the elements to be determined, the effect becomes a major limitation to the analytical sensitivity which can be achieved. For example, there are many problems of current technological interest which involve the study of impurities and dopants in specific semiconductor materials. In our experiment, the minimum detectable limit for measuring Cu in GaAs was increased by a factor of ten relative to that predicted on the basis of extrapolations which did not include the effects of resonant Raman scattering.
BACKGROUND

Raman scattering is an inelastic scattering process in which the energy loss experienced by an incident photon is equal to the energy difference between excited states of the target atom. X-ray Raman scattering is normally a weak effect relative to the elastic Rayleigh or inelastic Compton scattering typically considered in energy dispersive x-ray fluorescence analysis (8). However, if the energy of the incident photon is near a major absorption edge, a resonance effect is observed and the intensity of the Raman component increases until it can become the dominant source of scattered radiation. This effect was first observed by Sparks (9) using a fixed energy source and has been extensively studied by others using tunable synchrotron radiation (10,11).

Figure 1 is a schematic energy level diagram showing the relationship between the scattered photon energies and the atomic energy levels involved in Raman scattering. A simplified case in which only the K and L shells are involved is considered. The scattering involves a second order process (12) in which the energy lost by the scattered photon is transferred to an inner shell electron which is ejected to an unbound state leaving an inner shell vacancy in the atom. Since a continuum of unbound intermediate states is available for the two-step process, the resulting energy loss spectrum exhibited by the scattered photons is continuous with a maximum energy equal to the incident energy minus the L shell binding energy. For energies directly below a major absorption edge, the process is resonantly enhanced and the cross section increases dramatically. As the incident energy is increased above the absorption edge, the process is superceded by normal photoelectric absorption (11).
EXPERIMENT

Measurements were performed as part of an experimental program involving the development of optimal methods for synchrotron x-ray fluorescence analysis. Data were obtained using the LBL/Exxon 54 pole wiggler beamline at the Stanford Synchrotron Radiation Laboratory. A double-crystal (220) silicon monochromator was used to obtain variable energy incident photons. Energy dispersive x-ray fluorescence spectra were acquired using a \( 80 \text{ cm}^2 \) Si(Li) detector placed at 90° with respect to the beam in order to minimize Compton scattering. The samples were single-crystal, Czochralski-grown GaAs wafers. Spectra were obtained for several excitation energies below the Ga and As k-absorption edges at 10.37 and 11.87 keV respectively. Figure 2 shows logarithmic plots of three such spectra obtained at 9.20, 9.80, and 10.00 keV. Each spectrum was acquired for an equivalent amount of integrated charge from the ionization chamber which was used to monitor the incident x-ray flux. The amplitude of the resonant Raman scattering relative to the sum of the elastic Rayleigh scattering and inelastic Compton scattering peak increases as the energy of the incident radiation approaches the absorption edge energies. The energy separation between the elastic scattering and the high energy cutoff of the Raman continuum remains constant. At 10.00 keV the ratio of the integral of the continuous distribution relative to the area of the combined Rayleigh-Compton scattering peak is 2.31; at 9.20 the ratio is 0.64. The minimum detectable limits calculated for the case of Cu in GaAs are 1.0 ppm at 10 keV incident energy and 0.6 ppm at 9.2 keV.

Figure 3 shows a comparison between the scattered background obtained at 10 keV for the case of the GaAs sample and a light element cellulose matrix. The data obtained with the cellulose matrix are normalized to the elastic and
inelastic Compton scattering distribution for the GaAs case in order to illustrate the increase in continuum scattered intensity resulting from the resonance Raman scattering. Comparisons of the background contributions at the Cu k-alpha energy indicate that the minimum detectable limit for the measurement of Cu in GaAs is increased by a factor of 12.9 by the presence of the resonance scattering. For 9.2 keV excitation, the degradation is approximately four times.

CONCLUSION

The phenomena of resonant x-ray Raman scattering represents an important limiting factor in achieving optimum sensitivity for x-ray fluorescence analyses in cases where the excitation energy is selected to lie directly below an absorption edge of a major matrix constituent. This situation is likely to arise in measurements involving tunable monochromatic synchrotron radiation where sensitivity enhancement for specific elements and discrimination against major matrix components is desired.

ACKNOWLEDGMENT

The authors would like to thank W. Searles for his assistance in designing the experimental apparatus used in these investigations, and Dr. E. Bourret for the Cu-doped GaAs samples.

This work was supported in part by the Director's Office of Energy Research, Office of Health and Environmental Research, U.S. Department of Energy under Contract No. DE-AC03-76SF00098; and at SSRL, partially by the Office of Basic Energy Sciences, U.S.D.O.E., and partially by the National Institutes of Health, Biotechnology Resource Program, Division of Research Resources.
LITERATURE CITED


FIGURE CAPTIONS:

1) Energy level diagram for x-ray Raman scattering.

2) X-ray spectra obtained from single crystal GaAs showing variation in the resonant Raman scattering distribution for three excitation energies below the Ga and As k-absorption edges. The highest energy peak in each spectrum is the combined Rayleigh and Compton scattering peak.

3) X-ray spectra comparing the scattering distribution from GaAs relative to a hydrocarbon matrix. The two spectra are normalized to an equivalent cross section for elastic and inelastic Compton scattering.
\[ h\nu' = h\nu_o - \Delta E \]

Fig. 1.
Fig. 2.

a) $E_0 = 10.0$ keV
b) $E_0 = 9.8$ keV
c) $E_0 = 9.2$ keV

AR K-XRAYS

ENERGY (keV)

RELATIVE COUNTS