OBSERVATION OF X-RAY RESONANT RAMAN SCATTERING:
THE EARLY DAYS

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My early observation of resonant Raman scattering came as a serendipitous by-product of our
efforts to achieve the best possible signal for x-ray fluorescent analysis. We were also
investigating the x-ray spectrum produced by a monochromatic x-ray beam striking metal
targets which might contribute to the inelastic background. This background could contaminate
the very weak diffusely distributed elastically scattered radiation associated with defects in the
perfect periodicity of crystals. Energy analysis of the x-ray spectra created by monochromatic
Cu Kα and Mo Kα radiation impinging on highly pure metal targets showed an inelastically
scattered intensity related to the energy difference between the exciting radiation and the nearest
bound state. Confirmation of these observations and availability of synchrotron radiation has led
to wide application of this new x-ray spectroscopy in atomic physics including its use as a probe
of the unoccupied density of states.

1. The Early Experiment

1.1 Introduction

The discovery of radiative resonant Raman scattering\textsuperscript{1,2} occurred while we were
researching the radiative contributions to background when measuring very weak
and diffusely distributed x-ray scattering. The weak diffusely-scattered radiation
from crystalline Cu bearing alloys irradiated by monochromatic Cu Kα x-rays was
slightly too intense to be accounted for by the known elastic and inelastic
(Compton) scattering processes. Trace impurities could contribute fluorescent
radiation which was not discriminated against by our scintillation and proportional
counters. Funding for environmental science led to a research program to
determine the minimum detectable limit for trace elemental contaminants by x-ray
fluorescent analysis. A recently developed Si(Li) solid state detector to analyze
the radiation spectrum excited by Cu Kα and Mo Kα radiation was central to the
research.

1.2 Experimental Set-up

Our experiment was optimized to detect weak diffuse scattering associated with
measurements of short-ranged atomic arrangements and atomic-size
displacements in crystalline solid solution alloys\textsuperscript{3,4} as shown schematically in
Fig. 1. A large solid angle of characteristic Cu Kα radiation from a sealed Cu
anode x-ray tube was intercepted by a doubly-bent highly oriented graphite
monochromator and focused to a line at the sample.\textsuperscript{5} A Ross balanced filter pair
was used to remove the bremsstrahlung subharmonic x-ray energies diffracted by
the monochromator. High-purity Al covered all surfaces to reduce background
contamination by scattered or fluorescent radiation from other sources around
the sample. A drawing of the x-ray goniometer is shown in Fig. 2. The angle \( \Theta \)
defined in Fig. 1 is the same as the goniometer angle 20 of Fig. 2. Details are
given in Ref. 7.
Fig. 1. Experimental arrangement was designed to maximize the monochromatized radiation to the sample and for detection of a large solid angle.

Fig. 2. Samples were located on the axis of a $\theta$, $2\theta$ ($\Theta$) goniometer so that the radiation angle of incidence equals the angle of reflection. This geometry keeps the correction for radiation absorption in the sample angular independent. Collimation limited the field of view of the detector to just the sample.

Significant effort was made to both understand and minimize the background contributions to the spectra. The background contributed by the Si(Li) detector for this experimental arrangement was measured with doubly monochromatized Cu and Mo $K_\alpha$ x-rays. In the latter case a LiF (200) crystal set to Bragg-diffract Mo $K_\alpha$ x-rays replaced the sample and directed the x-rays into the Si(Li) detector. Shown in Fig. 3 is the spectrum recorded for Mo $K_\alpha$ x-rays. Si $K_\alpha$ radiation of 1.74 keV produced by the 17.44 keV Mo $K_\alpha$ radiation escapes the Si diode and reduces the energy deposited by 1.74 keV resulting in the familiar Si escape peak. The long flat background had been minimized with a collimator at the Si diode to prevent radiation from falling near the edges of the diode which contributes to insufficient charge collection. Electron noise causes the upturn in the spectrum at the lowest energies.

1.3 Radiation Spectra from High-Purity Elements

Our main research goal was the fluorescent detection of trace elements in water and air; hence, we used high purity substrates such as Si and Ge crystal wafers on
Fig. 3. Spectrum generated in a Si(Li) detector by a doubly diffracted monochromatic source of Mo $K_{\alpha}$ x-rays shows the familiar Si $K_{\alpha}$ escape peak. Au fluorescence from the voltage contacts on the Si diode, and the typical flat background associated with insufficient charge collection in the Si diode.

which a residue from evaporated water and air samples was deposited. Bragg diffraction from the wafers was avoided by cutting the crystal so that there were no lattice planes parallel to the surface. The Si substrates excited with either Cu or Mo $K_{\alpha}$ radiation gave the expected K fluorescent and scattered incident radiation and a featureless background like that shown in Fig. 3. Spectra from Ge substrates excited with Cu $K_{\alpha}$ radiation gave the expected scattered Cu $K_{\alpha}$ radiation and Ge K fluorescence excited by multiple x-ray energies selected by the higher-order graphite Bragg reflections from the bremsstrahlung produced in the x-ray tube from 40 keV electrons.

An unexpected asymmetric broad maximum ~ 1.2 keV below the energy of the incident Cu $K_{\alpha}$ radiation impinging on a Ge target is shown in Fig. 4. This broad maximum starting at ~ 7.0 keV and extending below 5 keV was not caused by the multiple x-ray energies passed by the monochromator as verified by taking the difference between the two measurements made with the Ni and Co filters. Their thicknesses are chosen to match their photoelectric linear absorption coefficients at twice the energy of the 8.04-keV Cu $K_{\alpha}$ radiation. The spectra of Fig. 4 are offset in energy to show that the filters are balanced in that the Ge $K_{\alpha}$ fluorescence excited by radiation having energies above the Ge K edge is the same in both spectra. The intensity difference between the two measurements is the scattered radiation from x-rays diffracted by the monochromator between the Co K absorption edge at 7.71 keV and the Ni K edge at 8.33 keV and brackets the 8.04-keV Cu $K_{\alpha}$ radiation. A similar measurement on the Ge sample with monochromatic Mo $K_{\alpha}$ radiation and yttrium oxide-Zr Ross balanced filter pair did not produce the broad maxima near 6.8 keV found with Cu $K_{\alpha}$ excitation. Therefore, the maxima was not the usual fluorescence from impurities. A
possible explanation was that the broad maximum arose from bremsstrahlung given off by deceleration of photoejected L shell electrons from Ge. The intensity would start at an energy shifted down by the binding of the L shell. The scattering intensity was angle-insensitive and unpolarized as expected of bremsstrahlung. The resonant character of this radiation discovered later removed this possibility.

A Cu single crystal was placed in the beam because of concerns about the excess diffuse scattering of Cu Kα radiation from Cu-bearing metal alloys. More intense inelastic scattering than found in Ge was observed about 1 keV below the energy of the incident Cu Kα x-rays, Fig. 5. The intensity and energy of the inelastic scattering features were found to be insensitive to the scattering angle θ (momentum transfer); this ruled out Compton scattering as a possible source. The energy of the Compton peak labeled $E_C$ in Fig. 5 is too close to the incident energy to be separated by the energy resolution of the Si(Li) detector, ~190 eV at 5.9 keV. This observation on Cu supported our earlier suspicions of an excess diffuse intensity. Perhaps it was to be a real effect. This inelastic radiation was not observed in Si but appeared from Ge and with

![Elastic Scattering](image)

Fig. 4. X-ray energy spectrum from Ge excited by Cu Kα x-rays with enough higher energy subharmonic x rays to produce the Ge Kα peak. Below the energy of the Cu Kα radiation is a broad asymmetrical inelastic scattering maximum.
even more intensity from Cu; therefore, most all of the metallic elements between Si and Mo were measured. Nearby elements with K shell binding energies closely below that of the 8.04-keV Cu $K_{\alpha}$ line contributed such intense fluorescence that any weak inelastic scattering would have been lost in the background generated in the Si(Li) detector. Those elements with K shell binding energies just above the 8.04-keV Cu $K_{\alpha}$ radiation produced measurable signals, as shown in Fig. 6. All the elements were irradiated with the same incident flux of Cu $K_{\alpha}$ x rays. The inelastically scattered intensity, increasing with atomic number, showed a resonance effect related to the energy difference between the exciting radiation and the binding energy of the K shell. In addition the energy downshift of this inelastic radiation was similar to the binding energy of the L shell. Since the intensity of the radiation resonantly depended on the proximity of a bound shell, other elements were chosen such as Ta where the L$_3$ shell at 9.88 keV is close in energy to the Zn K shell at 9.66 keV. Resonance emission from the Ta L$_3$ level was observed, as shown in the

![Graph showing energy levels and resonance effects](image)

**Fig. 6.** The intensity of the inelastic scatter was found to increase in resonance with the decreasing energy difference between the exciting and nearest but higher energy bound electron state of the sample. The energy loss was that required to promote an electron into the continuum and to leave the atom with a hole in the next lower bound shell.
bottom panel of Fig. 6, with an energy downshift near to the binding energy of the M shell. Thus it seemed that the most likely final state of the atom after the inelastic resonance emission is a hole in the next less tightly bound shell as shown in Fig. 7. This understanding was tested on several elements including the use of Mo K\(_\alpha\) x rays on Nb and Zr as shown in Fig. 8. Here the energy shift in the inelastic resonant scattering determined by the > 2-keV binding energy of the L shell is large enough to separate it from the K\(_\alpha\) fluorescence excited by the higher-energy contamination of the incident beam. These observations convinced me that the inelastic resonantly scattered intensity obeyed rules similar to those for characteristic fluorescence in that not only L transitions but M and higher-shells transitions would occur with lesser probability. Thus, it seemed that the excited bound K electron in near resonance with the incident x-ray energy permitted an L-shell electron to fall into the K-shell hole. Thus the K electron must be in a virtual excited state without enough energy to be photoejected from the atom. Or enough energy was transferred by the K electron to place the L electron into a virtual state. In either case the energy of the incident photon was down-shifted by the binding energy of the next higher shell. Because of the insufficient energy resolution of the Si(Li) detector, the inelastic resonance scattering associated with the weaker transitions from shells removed by two from the resonantly excited shell could not be resolved in energy.

![Fig. 7 Creation of the inelastic resonant scattering photon \(hv\) by the process of a photon \(hv\) creating a K hole filled by (unfortunately) an L\(_1\) electron in this early drawing.](image)

An experiment was designed to improve the energy resolution to study the fine structure with the use of a LiF (200) single-crystal monochromator for an energy resolution of ~8 eV at 8 keV. Even with the use of a 5-kW rotating anode and a spectrum acquired for ~20 hours, the statistics were inadequate to assess the fine structure with certainty. Better energy resolution and intensity was soon to become available from the synchrotron radiation sources.

![Fig. 8. Observation of the K-L inelastic resonant scattering in Zr and Nb excited by Mo K\(_\alpha\) radiation.](image)
2. Search for Similar Observations

A literature search for observations of similar energy shifted radiation started with the book by Compton and Allison\(^8\) which was a useful review of the literature on the interactions of x-rays with matter to the year 1936. A. H. Compton had predicted the inelastic (Compton) scatter from bound electrons with a minimum energy loss equal to the binding energy of the bound electron.\(^9\) Observation of this scattering was first reported by Davis and Mitchell in 1928 where Mo K\(_\alpha\) scattered by C was downshifted in energy by the C K shell binding energy.\(^10\)

This scattering was more clearly observed by Das Gupta in 1959 and called Smekal-Raman scattering.\(^11\) Das Gupta referenced Smekal\(^12\) as the first to theoretically predict this scattering as his paper preceded Compton's by one year; hence, the Smekal-Raman designation. Confirmation by Suzuki in 1964 appeared in the English literature in 1967 under the title "X-Ray Raman Scattering."\(^13\) A third confirmation by Faessler and Mühle was reported in 1966.\(^14\) Though this radiation was shifted by the energy of a bound electron, it was not resonant dependent. It did have a lower energy tail much like my observations, but the intensity increased with scattering angle unlike the resonant scattering. The radiation that I was concerned with was different.

X-ray plasmon scattering had also been predicted\(^15\) and observed.\(^16\) As there is no observed resonant behavior, and both the energy shift and intensity change with momentum transfer, plasmon scattering was not consistent with the observations of resonant scattering.

Reports of a radiative Auger effect in X-ray spectra from S excited by Cr K\(_\alpha\) radiation by Åberg and Utrainen\(^17\) showed an unexplained weak broad maxima that could be attributed to S K\(_\alpha\) radiation undergoing an inelastic resonant scattering with the S K shell. In this case, the S K\(_\alpha\) radiation was shifted down in energy by the binding energy of the L shells. However, there was no information on the resonant or momentum transfer dependence.

I turned to the electron spectroscopy literature to determine if the photoelectron spectra from samples excited below threshold had a maximum intensity at zero kinetic energy. A photoelectron maxima at zero kinetic energy would arise from those electrons which correspond to the resonant radiation maximum at the energy difference between the incident minus the L binding, \(E_i - E_L\). This electron intensity maxima at zero energy would be followed by a descending tail of electrons with increasing energy. Admittedly this is an unusual measurement in electron spectroscopy, and no such spectra were found.

Convinced that this inelastic resonant scattering was not previously reported and that it was a repeatable, thus verifiable observation, I gave the first paper on these findings at the IX International Union of Crystallography Congress and General Assembly in Kyoto, Japan, August 1972. As I did not feel comfortable about my understanding of the physics behind this resonant inelastic scatter, I presented the results and pointed out the similarities to the real part of the frequency dependent dispersion corrections to the x-ray atomic scattering factor, \(f(h,E) = f_0(h) + f(E) + f^*(E)\).
As an experimentalist more familiar with the crystallographic aspects of x-ray scattering, the strong relationship between the real part $f'$ of the x-ray resonant scattering term and the observed inelastic resonant scattering was most apparent. The resonant x-ray scattering terms are not sensitive to momentum transfer in the dipole approximation, and the amplitude $f'$ for a single oscillator of strength $g_K$ and binding energy $E_K$ with incident radiation $E_i$ has been given in wave-mechanical theory by James\textsuperscript{18} as

$$f'_k = g_k f\left(x^2 - 1\right)$$

where $X = E_i/E_K$. Values of $g_K$ given by Cromer\textsuperscript{19} were ~ 1.3 for the Ni-Ge series of the periodic table. To scale the value of $f'_k$ to the observed values of the inelastic resonant intensity and compare the frequency dependence of the observed inelastic resonant scatter to $f'_K$, I chose $g_K = 0.5$ with the results shown in Fig. 9. Though the magnitude was scaled to fit the data, the fit to the frequency dependence strengthened my belief in the similarity between the two. As the intensities had been converted into units of the Thomson scattering from a free electron, eu, by comparison with a previously calibrated scatterer of polystyrene,\textsuperscript{2} I sought to find a way to fit these absolute values.

The resonant elastic x-ray scattering process removes energy from the elastically scattered beam in a process where the initial and final state of the atom are the same. To account for this energy removal, I reasoned that since energy needs to be conserved the inelastic resonant scatter might account for some of that loss. At some intermediate step the incident radiation was transformed to an inelastic scatter with the atom left with a hole in the L or M shell for example when the incident energy is near resonance with a K shell.

In 1973 I had the opportunity to talk with Jan Korniga,\textsuperscript{20} a theoretical physicist at Ohio State University. We discussed this inelastic resonant scatter, and it similarities to the real part of the resonant terms in the x-ray atomic scattering factor. Korniga concluded that the resonant scattering could be accounted for by the P-A term of the interaction Hamiltonian taken to second-order in perturbation theory. This is also the explanation for the resonant terms $f'$ and $f''$ of the x-ray atomic scattering factor.\textsuperscript{21}

As I did not find any theoretical colleagues to seek the quantum-mechanical explanation of the observations, I developed a simple ad hoc theory based on
energy conservation similar to that used for the $A^2$ term. The argument is that in classical theory scattering from a collection of electrons is equal to the total scattering, elastic and inelastic that would be calculated by the quantum theory under certain assumptions. These assumptions are that interactions between electrons and exchange terms can be neglected. As the inelastic radiation is incoherent, the intensity from each participating electron can be added. With the assumption that all the elastic events lost to $I'$ contribute to the resonant Raman scattering, we have that the resonant intensity in eu per atom $I_{eu}$ is given by

$$I_{eu} / N = \sum_{k} \left| f_{ki} / n_k \right|^2 ,$$

(2)

where the sum is over those electrons in resonance with the incident energy, for example the two K shell electrons. This is a rough approximation as the measured inelastic intensity was only integrated between 4.8 and 7.3 keV which neglects the long Lorentizen tails and transitions such as K-M. On the other hand, approximately one-half the resonant events decay by Auger electron emission and don't contribute to the inelastic scatter. With this approach, I calculated the intensity of the inelastic resonance scattering and compared it with observations.\textsuperscript{1} Table 1. The fit was rather good. Compton intensities were also calculated to compare their relative contributions to the scattering process. The inelastic resonant scattering becomes much larger as the absorption edge energy is approached by the incident energy. The difference between incident energy and the resonant-shell binding energy is denoted by $\Delta E$ in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>$\phi$ (deg)</th>
<th>Compton$^a$ (eu/atom)</th>
<th>$\Delta E$ (eV)</th>
<th>Inelastic resonant scattering</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Obs. (eu/atom)</td>
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<tr>
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<td>12.14</td>
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<td></td>
</tr>
<tr>
<td>Cu</td>
<td>30</td>
<td>4.47</td>
<td>938</td>
<td>2.5±0.4</td>
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</tr>
<tr>
<td>Zn</td>
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<td>4.61</td>
<td>1618</td>
<td>1.3±0.5</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>12.21</td>
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</tr>
<tr>
<td>Ge</td>
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<td>5.23</td>
<td>3062</td>
<td>1.1±0.4</td>
</tr>
<tr>
<td></td>
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<td></td>
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<tr>
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<td>30</td>
<td>8.18</td>
<td>L$_3$ 1840</td>
<td>7.0±1.5</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>21.43</td>
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</tbody>
</table>

Now convinced that the experimental evidence was overwhelming, I felt that this observation should be published even though my theoretical insight into the absolute intensities was admittedly ad hoc. Perhaps others would be motivated to place these observations on a firm theoretical footing and bring new insights to the phenomena.

3. Confirmation and Early History

The first response to my July 1974 Phys. Rev. Lett. was a February 1975 Phys. Rev. Lett. by Bennett and Freund that confirmed the theoretical interpretation in terms of the $P\cdot A$ term taken to second order. These authors named the inelastic resonant scattering “Resonant X-Ray Raman Scattering” and successfully fitted the shape of my published spectrum from Ni as shown in Fig. 10. The term Raman was used to denote that the radiation was inelastic. This was followed by Eisenberger, Platzman and Winick with the first synchrotron-radiation experiment on the effect published in March 1976. In this first experimental confirmation, the observed similar spectra in Cu metal excited by monochromatic synchrotron radiation. Eisenberger et al. were able to measure both the peak position and intensity versus the energy of the incident radiation and fit their observations with the $P\cdot A$ term to second order. In addition, they found the resonant Raman line width narrowed in energy as the incident radiation approached the absorption edge, as predicted by theory. Bennett et al. published again in April 1976 with measured spectra excited by Cu Kα radiation in elements Ni, Zn and Ge which agreed well with my earlier observations in both intensity and energy. In addition they presented experimental evidence for what they called the infrared divergence of the Compton effect. In this process, an L-shell electron absorbs varying amounts of energy from the incoming Cu Kα radiation. The energy absorbed by the L electron increases on approach to the photoelectric limit and the cross section for the emitted radiation diverges on approach to zero energy. This insight based on the theoretical work of Gavrila and coworkers accounts for the extended low energy tail which becomes more pronounced as the incident energy moves away from resonance. The emitted radiation reaches a plateau before diverging into the

![Graph showing energy vs. peak position](image-url)
infrared where the emitted photons approach zero energy. The preceding two papers by Bannett and collaborators were expanded upon in a paper in 1977.26 Resonant Raman scattering from the filling of a K hole by an M electron was observed by Kodre and Shafr~th27 and published in 1979. They found that the K-M transition was similar to the K-L resonant Raman transition but with about 1/5 the intensity. This would be expected from the characteristic fluorescent yield of Kβ to Kα. Independently Suortti29 reported in 1979 evidence for the K-M as a contribution to the K-L scattering in an expanded experimental measurement of the resonant Raman scattering cross section. Suortti's values matched those previously observed experimentally for Cu metal with Cu Kα incident radiation.1,26 His calculation of the resonant Raman cross section based on its contribution to the absorption coefficient below the edge agreed well with his observations. In another paper in 1979, Suortti29 related the resonant Raman contribution to the absorption edge below threshold to if" through the optical theorem.

Coincident with the radiative resonant Raman scattering experiments, the radiationless Auger analog was being studied by Crasemann and his students with synchrotron radiation.29 They reasoned that not all the virtually excited electrons would decay with the emission of radiation. Auger electrons contribute the alternative channel for decay. They showed that the L3-M4 M5 (1G4) Auger electron emission broadened in energy as the incident photon energy is moved below the Xe L3 edge. The linear dependence of the spectator Auger satellite energies on incident photon energies signaled a resonance dependence. Earlier Eberhardt et al.30 resonantly excited electrons into unfilled bound states but were not searching for the radiationless analog to the radiative resonant Raman scattering.

The picture of the resonant Raman scattering that emerged is shown schematically in Fig. 11. Since the incident photon energy is less than threshold, only those electrons in the Lorentzen tail bound with lesser energy can be excited into unfilled bound states above the Fermi energy EF and beyond. Thus the electron carries away an energy distribution which resembles the Lorentzen

![Diagram of resonant Raman scattering](image)

**Fig. 11.** Diagram of the picture that emerges for the resonant Raman scattering process. An incident photon hv with an energy less than that for the K bound state excitons electrons in the Lorentzen tail to unfilled bound states and beyond. The filling of the virtual hole by the L electron creates the resonant Raman photon hv.
Therefore, the outgoing resonant photon has a maximum energy of $E_{hv'} = E_{hv} - E_L$ in this case, and an intensity distribution which follows a Lorentzian shape towards lower energies. As the incident photon energy rises towards threshold, the resonant peak narrows to a minimum.

4. Conclusion

This historical note on the early observation of the resonant Raman scattering covers the literature to 1980 - the first six years after discovery. Since then the literature has grown rapidly, and there are more recent reviews. A recent book that covers aspects of x-ray resonant scattering ranging from the crystallographer's point of view to that of the spectrosocist's is reference 31. Most recently Crasemann\(^3\) has given a very readable review of the historical perspectives of resonant Raman transitions. The Proceedings from the present conference will include the latest insights and will help bridge the gap from the optical through the soft to the hard x-ray energy spectroscopies.

Acknowledgments

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