# Relation between X-Ray-Raman and Soft-X-Ray-Absorption Spectra

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A spectrum of x-ray inelastic scattering of copper $K\alpha_1 K\alpha_2$ radiation scattered by metallic lithium through $2\theta = 115°$ was obtained. (These conditions correspond to a momentum transfer $k = 6.87 \times 10^{10}$ m$^{-1}$.) The spectrum is compared quantitatively to an experimental soft-x-ray-absorption spectrum of lithium. This comparison serves as an experimental verification of the relation between x-ray-Raman spectra and soft-x-ray-absorption spectra. The method renders possible the study of solid-state effects via x-ray Compton-Raman experiments without *ad hoc* assumptions concerning the wave functions of the inner electrons. Also presented is some evidence of the failure of a random-phase approximation and the impulse approximation in the region under investigation.

## INTRODUCTION

Current interest in x-ray Compton-Raman scattering is focussing on the study of solid-state effects (e.g., the many-electron problem) and collective excitations (plasmons). A goal in x-ray inelastic scattering has been the experimental determination of the two-dimensional electron momentum distribution (EMD) of the valence or conduction electrons and, in turn, the experimental study of the spatial part of the electron initial-state wave function. For EMD studies, the experimental conditions are usually so arranged that the energy transfer to the electron is much larger than the electron binding energy, and the momentum transfer $k$ is much larger than the inverse of a characteristic orbital radius $r$ of the bound electron

$$k \gg 1/r \ .$$

Under these conditions, the final state of the scattering electrons is a plane wave and the Compton profile depends only on the ground-state wave function of the scattering electrons. Within these limits, and assuming a one-electron approximation, the "impulse-approximation" approach[1] is valid. It is within this area that much of the Compton scattering work has been done to date. The properties of electrons in solids, however, can be better understood in the region of smaller energy and momentum transfers. X-ray Compton spectra are very sensitive to band structure near the Fermi level. We therefore chose to work in a momentum-transfer region $k < 7 \times 10^{10}$ m$^{-1}$, $\vec{k} \cdot \vec{r} < 1.4$, where we can illustrate the method under consideration as well as learn more about the solid-state physics of the problem.

Lithium metal was chosen for a scatterer since it is an interesting (although relatively complicated) low-$Z$ solid for study, and much Compton work[2–19] has been done on this material in the past. In the small-momentum-transfer region $k \lesssim 1$, plasmon excitation in lithium has been observed.[9,14,15] In the region of large momentum transfer, momentum distributions have been derived.[8,10,11] In the range in between, several interesting features have been noted, the most important of which is the appearance of the x-ray Raman effect.[3,7,12] While Compton scattering depends strongly on angle, Raman scattering is almost independent of angle. The phenomenon one observes in x-ray scattering is a superposition of both Compton and x-ray Raman scattering—hence the terminology "x-ray Compton-Raman scattering." Table I shows, for each of the above references, what the values of $|\vec{k}|$ and $\vec{k} \cdot \vec{r}$ are, and what type of study was made. We note particularly the work by Suzuki,[7] whose experiment is very similar to our own (Cu$K\alpha$ scattered on lithium through $2\theta = 120°$), which demonstrated the same broad features we report here and analyze in detail.

## APPROACH TO THE PROBLEM

The greatest source of experimental uncertainty in both the intermediate and large momentum transfer areas is the subtraction of the core-electron contribution from the total profile of inelastic scattering. Customarily, the core profile is calculated and subtracted from the total profile, and the remainder is called the valence electron Compton profile. X-ray Compton spectra are very sensitive to the existence of holes in the core levels as well as being sensitive to band structure near the Fermi level. The main difficulty, then, in calculating the shape of the Compton profile is the problem concerning the behavior of electrons

TABLE I. X-ray Compton scattering measurements on lithium.[a]

| Author | Radiation | Angle ($2\theta$) (deg) | $k$ ($10^{10}$ m$^{-1}$) | $\hat{k}\cdot\hat{r}$ | |
|---|---|---|---|---|---|
| Kappeler (Ref. 2) | Mo$K\alpha$ | $\geq 9.1$ | $\geq 4.64$ | $\geq 0.928$ | |
| Das Gupta (Ref. 3) | Cu$K\alpha$ | 55 | 3.12 | 0.62 | Raman |
| Alexandropoulos, Alexopoulos (Ref. 4) | Cu$K\beta$ | 18 | 1.4 | 0.28 | |
| Cooper, Leake, | Mo$K\alpha$ | 90 | 12.5 | 2.5 | |
| Weiss (Ref. 5) | | 100 | 13.5 | 2.7 | |
| Theodossiou, | Cr$K\beta$ | 10 | 0.526 | 0.11 | |
| Vosnidis (Ref. 6) | | 18 | 0.945 | 0.19 | |
| | | 32 | 1.67 | 0.33 | |
| | | 45 | 2.31 | 0.46 | |
| Suzuki (Ref. 7) | Cu$K\alpha$ | 80 | 5.24 | 1.0 | |
| | | 120 | 7.06 | 1.4 | Raman |
| | | 140 | 7.66 | 1.5 | |
| Phillips, | Mo$K\alpha$ | 117 | 15.1 | 3.0 | EMD[b] |
| Weiss (Ref. 8) | | | | | |
| Priftis, | Cr$K\beta$ | 5 | 0.263 | 0.05 | |
| Theodossiou, | | 10 | 0.527 | 0.11 | Plasmon |
| Alexopoulos (Ref. 9) | | 15 | 0.789 | 0.16 | |
| Weiss, | Mo$K\alpha$ | 119 | 15.3 | 3.1 | EMD |
| Phillips (Ref. 10) | | | | | |
| Cooper, Williams, | Mo$K\alpha$ | 153 | 17.2 | 3.4 | EMD |
| Borland, Cooper (Ref. 11) | | | | | |
| Suzuki, Kishimoto, | Cr$K\alpha$ | 30 | 1.56 | 0.31 | |
| Kaji, Suzuki (Ref. 12) | | 60 | 3.02 | 0.60 | |
| | | 90 | 4.27 | 0.85 | |
| | | 120 | 5.23 | 1.0 | |
| | | 160 | 5.95 | 1.2 | |
| Alexandropoulos, | Cu$K\alpha$ | 90 | 5.77 | 1.15 | |
| Parks, Kuriyama (Ref. 13) | | | | | |
| Priftis (Ref. 14) | Cr$K\beta$ | 5 | 0.263 | 0.05 | |
| | | 10 | 0.526 | 0.11 | Plasmon |
| | | 15 | 0.789 | 0.16 | |
| Alexandropoulos (Ref. 15) | Cu$K\alpha K\beta$ | 7.7 to 1.2 | 1.1 to 1.0 to 0.95 to 0.895 | | Plasmon |
| | Cu$K\alpha K\beta$ | 10.4 to 3.8 | 0.80 to 0.70 to 0.60 to 0.40 | | |
| Currat, DeCicco, Weiss (Ref. 16) | Mo$K\alpha$ | 155 | 17.3 | 3.5 | |
| Phillips, Weiss (Ref. 17) | Mo$K\alpha$ | 158 | 17.3 | 3.5 | |
| Cohen, Alexandropoulos, Kuriyama (Ref. 18) | Cu$K\alpha$ | 25 | 1.76 | 0.353 | |
| Eisenberger, Lam, Platzman, Schmidt (Ref. 19) | ... | 170 | ... | ... | |

[a]We used $k = 4\pi \sin\theta/\lambda$, where $\theta$ is half of the scattering angle and $\lambda$ is the incident wavelength. The value of $r_{\mathrm{Li(1s)}}$ is given by J. C. Slater, in *Quantum Theory of Atomic Structure* (McGraw-Hill, New York, 1960), Vol. 1, p. 210.

[b]Electron momentum distribution.

slightly above the Fermi level in the presence of a localized hole in a lower level. (Similar difficulties arise in calculating the exact shape of a soft x-ray absorption spectrum.) It is especially desirable to determine these quantities experimentally in an effort to avoid ambiguities.

In principle, the current and density correlations of electrons in solids can be determined through

two simultaneous, independent experiments—x-ray absorption and x-ray Compton-Raman scattering. If the electrons are in a solid that is either isotropic, or alternatively has a high degree of symmetry, then it has been proven[20,21] that x-ray inelastic scattering is related[22] to x-ray absorption:

$$\left(\frac{d^2\sigma(\omega)}{d\omega d\Omega}\right)^{\text{inel}} \sim \frac{1}{\omega}\left(\frac{d^2\sigma(\omega)}{d\omega\, d\Omega}\right)^{\text{abs}} \quad \text{if } \vec{k}\cdot\vec{r} \lesssim 1, \qquad (1)$$

where $\vec{k}$ and $\omega$ are the momentum transfer and the energy transfer, respectively, and $r$ is the orbital radius of a bound electron. The validity of this relation has been proven via approximations in the calculation of the matrix elements,[20] and also from first principles using current conservation rules.[21,22] It has recently also been proven for x-ray inelastic scattering in the forward direction ($\vec{k}\cdot\vec{r} \ll 1$) by model calculations.[23] Suzuki[7] used relation (1) to confirm the existence of x-ray Raman scattering experimentally. Thus, this relation can be considered to be a general link between x-ray Raman and absorption spectra, regardless of one's choice of electron wave functions—a choice which can influence considerably the results of a calculation of these two spectral shapes.

Relation (1) can be used in two ways to study solid state effects on electrons. First, one can make use of the soft x-ray absorption spectrum due to the inner level electrons to obtain the outer electron x-ray Compton profile (provided that the two experiments are independent). The validity of the one electron model in solids, or many body effects, for example, could then be studied without making *ad hoc* assumptions about core electron wave functions. Conversely, x-ray Raman experiments may prove to be a solution to the many experimental difficulties encountered in preparing samples suitable for soft x-ray absorption experiments. The information obtained from x-ray Raman spectra arises from the bulk of the sample material, so surface states and impurities exert very small influence on the spectra. This is in sharp contrast to the case for soft x-ray absorption. The difficulties pertaining to obtaining a strong soft white x-ray source similarly do not exist in obtaining experimental x-ray Raman spectra. An important drawback to using x-ray Raman scattering experiments in place of absorption experiments lies in the fact that the energy resolution of the scattering experiment is inferior to that available now for x-ray absorption. One can reasonably expect, however, that the energy resolution will improve in the future.

## EXPERIMENT

In this work, the relation between x-ray Raman and soft x-ray absorption spectra is verified experimentally for metallic lithium. An inelastic scattering experiment was performed using copper $K\alpha_1 K\alpha_2$ radiation scattered through an angle of $2\theta = 115° \pm 1°$. These conditions correspond to momentum transfer $k = (6.87 \pm 0.019) \times 10^{10}$ m$^{-1}$, and $\vec{k}\cdot\vec{r} \sim 1.4$. The choice of sample and experimental conditions permit the verification of relation (1).

The double-crystal spectrometer and the data-analysis techniques were described in an earlier publication.[24] Corrections to the total experimental profile included: (i) a linear background subtraction; (ii) removal of the elastic scattering component of the spectrum; and (iii) a Fourier deconvolution of the inelastic scattering spectrum in order to correct for instrumental distortion. The experimental background was determined through long-time measurements beyond the short wavelength side and also beyond the long-wavelength side of the scattered spectrum. A straight line drawn through these points, passing under the scattering data, was taken to be the background. The total scattered spectrum, with the background subtracted, consists of elastic and inelastic scattering parts. The elastically scattered component (Rayleigh scattering) is, under these experimental conditions, well separated from the Compton-Raman component, rendering its removal a simple task. The copper $K\alpha_1 K\alpha_2$ fluorescence spectrum at $2\theta = 115°$, necessary for performing the Fourier deconvolution, was obtained under the same astigmatic conditions as the spectrum from lithium. The instrumental correction[25] is now standard in the field, and it will not be further discussed here.

The resultant inelastic scattering spectrum was compared to the soft x-ray absorption spectrum obtained by Baker and Tomboulian.[26] Their published data points were curve fitted to $e^{-x}$ on the long-wavelength side of the absorption peak. (The other side of the peak was left untouched.) Since the published data ends at 155 eV, the long-wavelength side of the absorption data was extrapolated, via the fitted curve, as far as the scattering data extended. Using Eq. (1), the core electron contribution was obtained by multiplying the soft x-ray absorption data by the inverse of the transfer energy and then by fitting the result to the structure of the total profile, thereby obtaining the normalization constant. The core-electron contribution (on an arbitrary intensity scale) is shown in Fig. 1, along with the x-ray inelastic scattering spectrum. The energy resolution in this experiment was 2.4 eV.

## DISCUSSION

In the present work, the prominence of the x-ray Raman is a distinct aid in carrying out the core-to-total profile normalization. At larger momentum transfers, the Compton and Raman components overlap, yielding the lithium Compton profiles

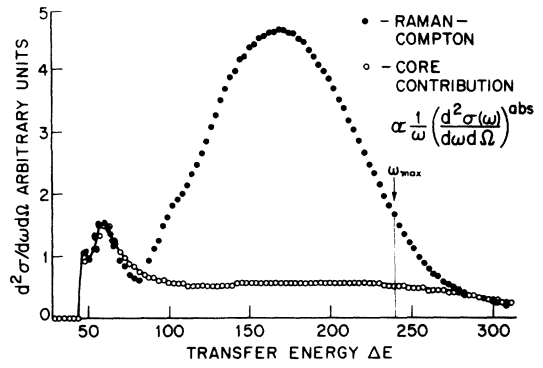


FIG. 1. Compton-Raman spectrum of lithium for $k = 6.87 \times 10^{10}$ m$^{-1}$. The spectrum was corrected for background, elastic scattering, and instrumental distortion, The core contriubtion, indicated with the open circles, was estimated using Eq. (1) and the soft x-ray absorption data of Baker and Tomboulian.

found in the literature, for example, in Refs. 8 and 16. We note again, however, that the structure (x-ray Raman) has been seen before, for example in Ref. 7, although with less experimental resolution. In this report, not only is the core contribution clearly visible, but there is also a strong indication of where the valence electron profile ends. The entire experimental profile after this point is expected to be due solely to the core electron scattering. This point, as predicted in a random-phase approximation (RPA) is indicated by $\omega_{max}$ in Fig. 1:

$$\omega_{max}^{RPA} = (k/k_F)^2 - 2(k/k_F) ,$$

where $k_F$ is the Fermi momentum and $k$, the momentum transfer, is as indicated above. It is evident that the valence-electron contribution to the total profile of inelastic scattering continues beyond the predicted cutoff point. The position of $\omega_{max}$ is found to be about 15% higher than the position predicted in the random-phase approximation. This is not the first time that a discrepancy has been found between predicted and measured values of parameters calculated through a random phase approximation. Such a discrepancy was reported in the prediction of the plasmon cutoff,[15,27] and in inelastic scattering experiments performed in the region of intermediate momentum transfer.[18] A recent letter by Kliewer and Raether[28] explains the apparent disagreement between theory and experiment through calculations involving a generalization of the Lindhard electron-gas dielectric function, which incorporates the effects of damping. The critical wave vector, which has been used to indicate that value of $k$ which separates low-$k$ collective effects and high-$k$ single-particle effects, is seen now as an indicator of the onset of strong plasmon damping. Significant collective effects persist to wave vectors beyond this critical value. They conclude that there is no definitive way to separate collective from single-particle effects for $k$'s larger than $k_{critical}$. It is reasonable to expect that a similar explanation will be forthcoming in the case of the present discrepancy.

Although no measurements were made for energy transfer $\Delta E > 320$ eV, it appears from Fig. 1 that the ratio of core-to-valence integrated profiles is not 2:1. In principle, one might expect that the areas under the respective profiles would be proportional to the number of electrons at each energy level participating in the scattering. It would appear that the scattering probabilities for electrons at different energies are not, necessarily, the same. It is not possible, here, to give the values for the experimental integrated profiles because the core electron contribution extends to very large energy transfer—beyond our experimental range.

The valence electron Compton profile of lithium, as found from the subtraction of the core electron contribution from the total profile, is given in Fig. 2. The scale was changed from $\Delta E$ to $q$ (atomic units) in the usual manner.[8] This profile was found to be unsymmetrical, having a half-width at half-maximum of $q = 0.240 \pm 0.018$ a.u. on the lower-energy-transfer side, and a half-width at half-maximum of $q = 0.272 \pm 0.018$ a.u. on the higher-energy-transfer side. Such asymmetry was noted, for example, in beryllium by Currat *et al.*,[29] who "symmetrized" their valence electron Compton profile by averaging the $\pm q$ sides before deriving electron momentum distributions. A similar asymmetry has also been noted in Be by Suzuki.[30] The impulse approximation does not appear to be an adequate description of the valence

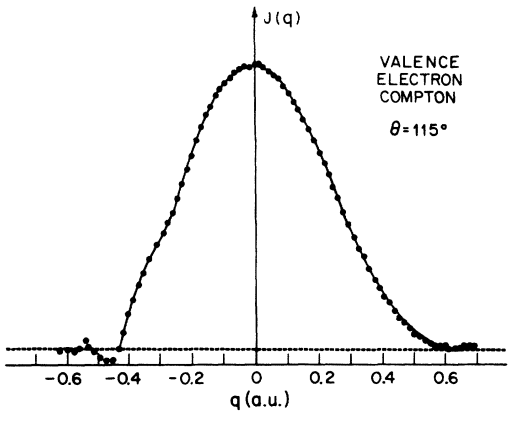


FIG. 2. Compton profile for lithium conduction electrons. The zero level for $J(q)$ is indicated by the dashed horizontal line.

electron Compton profile in this momentum-transfer region. (The impulse approximation cannot yield a nonsymmetrical profile.)

We note that Fig. 1 shows that the intensity of the core contribution, estimated from the absorption data, slightly exceeds the total intensity for inelastic scattering in the energy range around 75 eV, resulting in negative values of $J(q)$ at $q \sim -0.5$ (Fig. 2). This overestimation can be attributed either to an improper normalization of the absorption data or to a real effect which indicates the fact that the differential cross section for inelastic scattering cannot be given by a simple sum of core and valence contributions. The differential cross section contains a cross term involving both the core and the valence electrons, not necessarily being positive.

In conclusion, the present investigation confirms earlier theoretical predictions about the compatibility of soft x-ray absorption and x-ray Raman spectroscopy, and at the same time proves that Eq. (1) is valid for $\vec{k} \cdot \vec{r} \sim 1.4$, within the limits of experimental errors. Another conclusion is that previously reported asymmetries in the valence electron Compton profile of Be are also present in the case of Li, and that the simple random phase approximation does not predict, to better than 15%, some features of the Compton spectrum.

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[22] According to Ref. 21, one can write the transition probability $W$ for inelastic scattering as $W^{\text{inel}} \propto (|k|^2/\omega^2)\vec{s}\,\overleftrightarrow{J}\,(K_1, K_2)\vec{s}$ and the transition probability for photon absorption as $W^{\text{abs}} \propto (1/k_2)\vec{\epsilon}$. $J$ is the current correlation tensor, where a set of matrix elements is described by $\vec{\epsilon}\,\overleftrightarrow{J}\,\vec{\epsilon}$ and another set by $\vec{s}\,\overleftrightarrow{J}\,\vec{s}$. $\vec{\epsilon}$ is perpendicular to $\vec{k}$, while $\vec{s}$ is parallel to the vector $\vec{K}$. Thus, an x-ray-absorption experiment determines the matrix elements $J_{xx}(k_z,\omega)$ and $J_{yy}(k_z,\omega)$, while an inelastic scattering experiment gives $J_{zz}(k_z,\omega)$. Neither experiment alone determines the whole set of matrix elements $\overleftrightarrow{J}$, unless the system is isotropic or has a high degree of symmetry. In the present investigation, the tensor $\overleftrightarrow{J}$ is diagonal so that the ratio of inelastic scattering to absorption is equal to $1/\omega$.

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