

Neutron spin-up-spin-down measurements were made before and after the scan and show that the polarization recovered effectively. Selective depolarization of nuclei effectively combines diffraction and electron-nuclear double resonance¹¹ greatly expanding the information available from each Bragg peak. For sufficiently distinguishable resonances it performs a partial analysis of the diffraction pattern.

Other rf frequencies were fed into the coil corresponding to the nitrogen and lanthanum resonance values but no effect of their nuclear polarization was found either on the "hydrogenous" Bragg peaks or on "nonhydrogenous" peaks such as (0, 1, 2).

The nuclei may be polarized by other means than dynamic polarization, but the dynamic method has the advantage that a change from positive to negative nuclear polarization can be made easily. We think that the method may have some virtues for studying chemically interesting sites in complex crystals such as proteins.

We are planning to refine the evaluation of the position of the hydrogens in LMN by using a four-circle neutron-diffraction experiment, and to use the polarization data as a further refinement.

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Evidence of Optical Transitions in X-Ray Inelastic Scattering Spectra: Li Metal*

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We report results of x-ray Compton-Raman scattering experiments. In addition to the expected Compton and Raman scattering, there is a prominent feature in the form of a peak near $E/E_F = 1$. The new peak can be explained qualitatively by considering the conduction band of lithium metal to be composed of hybridized orbital electrons, and it furnishes the first evidence of an $L-x$ -ray Raman band.

The strongly interacting electron gas is one of the most interesting systems in solid-state physics, and it may soon be expected to form a rigor-

ous testing ground for approximations and theories. The numerous difficulties involved in the theoretical calculations render it one of the areas

in physics about which little is known. Experimentally, the best, if not the only, method of investigating this area is x-ray inelastic scattering. Here the spectra are functions of the energy, with the parameter $\vec{\kappa}$, the momentum transfer. A collection of a number of such spectra yields directly the energy-loss function (the dynamic structure factor^{1,2}). We define the momentum transfer by $|\vec{\kappa}| = |\vec{k}_{\text{in}} - \vec{k}_{\text{out}}| = (4\pi/\lambda_{\text{in}}) \sin(\varphi/2)$, and the energy transfer by $E = \hbar(\omega_{\text{in}} - \omega_{\text{out}})$, where the \vec{k} 's and the ω 's are the wave vectors and the frequencies of the incoming and the outgoing photons; λ_{in} is the incident wavelength, and φ is the scattering angle. The differential cross section for x-ray inelastic scattering is given^{1,3} by

$$\sigma(\vec{\kappa}, E) = -2C(k_{\text{in}}, k_{\text{out}}) \text{Im}(\vec{P} \cdot \vec{\epsilon}^{-1}), \quad (1)$$

where

$$C(k_{\text{in}}, k_{\text{out}}) = (2\pi)^{-4} (e^2/mc^2)^2 (\omega_{\text{in}} \omega_{\text{out}})^{-1} \\ \times (\vec{v}_{\text{in}} \cdot \vec{v}_{\text{out}})^2,$$

and the \vec{v} 's are the x-ray polarization directions. \vec{P} is the polarization propagator and $\vec{\epsilon}^{-1}$ is the inverse dielectric function. The differential cross section can also be written in terms of the electron correlation:

$$\sigma(\vec{\kappa}, E) \propto (\kappa/E)^2 \hat{s} \cdot \vec{J}(\vec{\kappa}, E) \cdot \hat{s}, \quad (2)$$

where \hat{s} is the unit vector in the direction of $\vec{\kappa}$, and J_{ij} is the Fourier transform of the current correlation $\langle \Delta j_i; \Delta j_j \rangle$. This expression establishes the relation between x-ray inelastic scattering and x-ray absorption spectra and leads to x-ray Raman scattering.

To get a complete picture of the interaction, it is necessary to achieve a collection of experimental spectra over the entire range of $\vec{\kappa}$ and E . This task is, however, a very difficult one because of the combination of the small interaction cross section and the requisite high resolution. Moreover, a most valuable contribution at present would consist of performing those measurements which can establish the regions of validity and the breakdown points of the few available theories.

In the region of very large momentum transfer,⁴ the spectra of inelastically scattered x rays and γ rays can be explained in a manner that satisfactorily establishes Compton scattering as a method for measuring electron momentum distributions and the spatial part of the electron wave function. A breakdown has been demonstrated in the random-phase approximation (RPA) in

the area of low and intermediate momentum transfers.^{3,5}

Although the theory of collective excitations explains quite well the scattering observed in the region of very small momentum transfer, there remain some problems relating to results in the neighborhood of κ_c , where plasmon features persist above the cutoff frequency.⁶ Discrepancies have also been reported⁷ where the disagreement with theory extended to the plasmon-lifetime predictions. Although some of these results can be explained through modifications of the RPA, one of the most recent experiments⁸ on the shape of the plasmon line of beryllium shows quite strong departures from RPA.

A most dramatic departure from RPA was discovered by the authors,³ reporting on x-ray scattering by lithium for $\kappa/\kappa_F = 1.59$ ($\varphi = 25^\circ$) in their attempt to study the complete behavior of the electrons of that element. The present investigation confirms those initial observations and fills in results to the upper limit of the intermediate-momentum-transfer region, but not beyond $\kappa/\kappa_F = 4.2$. Even at the upper limit, the departure from RPA exists, but we find the disagreement between experiment and theory to decrease with increasing momentum transfer.

The double-flat-crystal spectrometer used in these experiments has been described earlier.⁹ Copper $K\alpha_1, \alpha_2$ incident radiation was scattered by polycrystalline lithium at various scattering angles, corresponding to $\kappa/\kappa_F = 1.9, 2.5, 3.1,$ and 4.2 . A fluorescence spectrum of copper radiation was taken at these same angles, for each of the different experimental conditions. For scattering angle equal to 40° ($\kappa/\kappa_F = 2.5$), curves were taken with the sample in the transmission as well as in the reflection position in order to check for possible effects due to multiple scattering, or to surface treatment or impurities. All of the spectral features remained the same. Thus the two sets of data taken at 40° will be treated as one. The spectral response due to $K\alpha_1$ alone was obtained directly by subtracting, in the usual fashion, the $K\alpha_2$ response from the total spectrum. The results are shown by the solid lines in Figs. 1(b)–1(e). The resultant spectra can be divided into three parts: (i) a peak near $E/E_F = 1$, (ii) a spectral distribution around the expected Compton peak, and (iii) a spectral band around $E/E_F = 12$.

The third feature obviously corresponds to x-ray Raman scattering by the K -shell electrons of lithium.^{9,10} The spectrum in the central part

may be compared with Compton scattering by an electron gas. The differential cross section for an electron gas can be calculated from Eq. (1) and, in particular in RPA,² by replacing ϵ^{-1} by

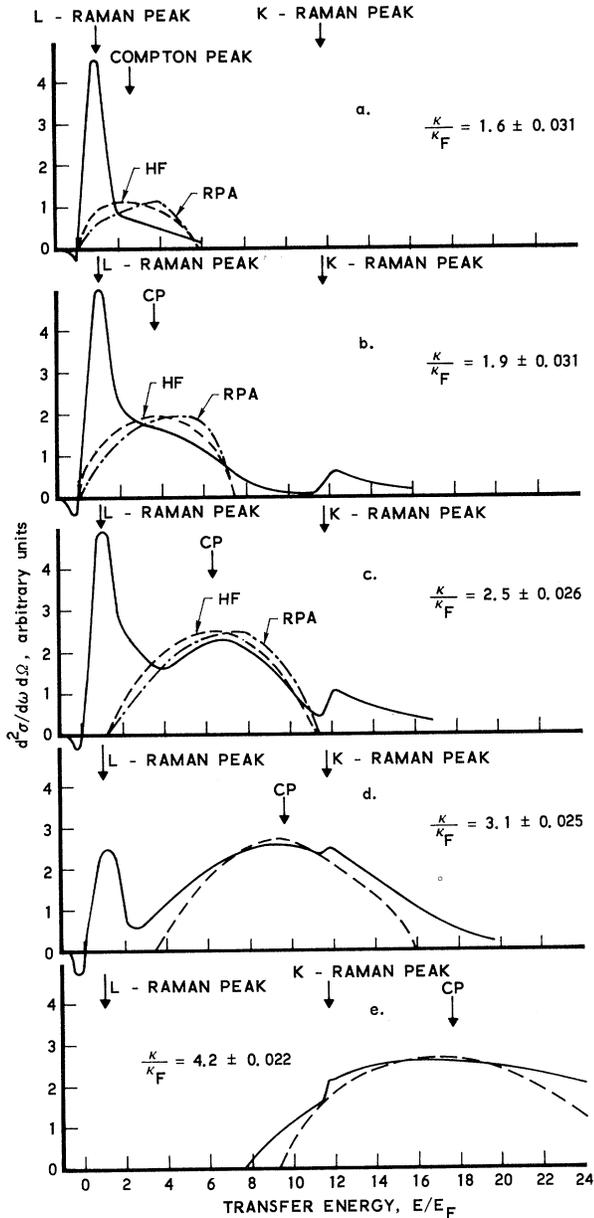


FIG. 1. The spectra (solid line) of x-rays inelastically scattered by lithium at $\kappa/\kappa_F =$ (a) 1.6, (b) 1.9, (c) 3.5, (d) 3.1, and (e) 4.2 (without correction for instrumental broadening), and the spectral distribution predicted by RPA and Hartree-Fock (HF) (dashed line) convoluted with our instrument function. Note the changes in the relative intensity of the peak at $E/E_F \approx 1$, compared with the spectral distribution in the region of the expected Compton band. "L" Raman refers to the optical transition. We used $\kappa_F = 1.1 \times 10^{10} \text{ m}^{-1}$ and $E_F = 4.7 \text{ eV}$.

the inverse of the Lindhard dielectric function.¹¹ We calculated this differential cross section at the different scattering angles and convoluted it with the spectral shape of the incident $K\alpha_1$ (obtained from the appropriate copper fluorescence spectrum). The results are shown by the dashed curves in Fig. 1 for both RPA and Hartree-Fock³ calculations. No attempt was made to normalize the curves. The prominent feature of the observed spectra is the sharp peak, almost resembling a line spectrum, near $E/E_F = 1$. Neither RPA nor Hartree-Fock calculations seem to explain this feature, nor does the electron gas seem to provide models for this phenomenon that takes place so prominently in the intermediate-momentum-transfer range.

The explanation that this feature may be an artificially introduced component of the spectrum has been ruled out after extensive tests. The spectral shape was found to be almost entirely independent of the run, the experimental background, and the normalization constant. When two sets of data, taken from the same scatterer, were used in the data reduction, the resultant spectrum was a flat line parallel to the energy axis. When the spectra of Cu $K\alpha$ fluorescence and x rays scattered by lithium were offset by an amount less than or equal to the corresponding experimental uncertainty in angle, the resultant spectral shape changed very little.

The spectra obtained at $\kappa/\kappa_F = 1.9, 2.5,$ and 3.1 thus confirm the earlier observation³ at $\kappa/\kappa_F = 1.6$ on the peculiar behavior of energy-loss spectra for low and intermediate momentum transfers. The results from all these spectra can be summarized as follows:

(1) As the momentum transfer becomes smaller, that is to say, as the scattering angles become smaller, the spectral distribution that is thought of as Compton scattering by an electron gas becomes less significant. The intensity ratio of the first peak N_p and the "Compton" band N_s is obtained from the spectra at the different angles as listed below (see Fig. 1):

N_p/N_s	κ/κ_F	φ (deg)
3	1.6	25
1	1.9	30
0.5	2.5	40
0.2	3.1	50
0	4.2	70

(2) This new peak appears when the spectrum also contains an x-ray Raman band due to the K

electrons of lithium. By contrast, the K -x-ray Raman band has been reported at larger momentum transfers without mention of the presence of this new peak.

These results may be explained qualitatively by considering an elementary excitation of electrons from the $2s$ valence-band-like state to the upper bound bandlike states. In other words, the new peak is caused by x-ray Raman scattering due to optical transitions (or absorption) between the $2s$ state and the upper bound states such as $2p$, etc. The differential cross section for x-ray inelastic scattering is related to the x-ray absorption cross section,² and the criterion for the appearance of the K -x-ray Raman band was previously determined¹⁰ to be $\kappa r_K \approx 1.4$. If this criterion holds for these optical transitions, then the "orbital" radius of the valence-band-like state, r_L , is estimated to be $(6.27/2.5)r_K \approx 2.5r_K$, where we chose $\varphi = 40^\circ$ as the practical upper bound for the appearance of this new peak. From this point of view, the new peak could appear at lower scattering angles than those angles for which the K -x-ray Raman band begins to appear. It is also satisfying to note that the energy loss of the x-ray photons due to these optical transitions should be of the order of the filled bandwidth, which is in agreement with the experimental peak position of $E/E_F \approx 1$ ($E_F = 4.7$ eV). The sharp peaking may be enhanced by the effects of the transitions involving the p states, as Mahan¹² and Nozières and DeDominicis¹³ have demonstrated in x-ray absorption and emission edges.

In conclusion, this Letter furnishes the first evidence of optical transitions in x-ray inelastic scattering spectra. The qualitative fit of the data by this interpretation is very satisfactory and may provide new insights into the important intermediate-momentum-transfer region of x-ray Compton-Raman scattering.

Note added.—Concurrent with the submission of this Letter, Ching and Callaway¹⁴ reported calculations indicating a peaking in the optical conductivity of lithium at about 4.5 eV, offering ad-

ditional support for the conclusions we reach from our experimental observations. Furthermore, even more recently Platzman and Eisenberger¹⁵ reported a feature in the inelastic x-ray scattered spectra from Be, graphite, and Al. Although their interpretation varies considerably from ours and the reported feature is quite faint, it appears in the same position as our new peak.

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