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X-Ray Raman and Compton Scattering in the Vicinity of a Deep Atomic Level

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In this Letter we report the first observation of inelastic x-ray scattering from an atom in which both Raman and Compton processes have been observed simultaneously. It has been observed that x-ray Raman and Compton scattering in the vicinity of a deep atomic level exhibit different behavior as a function of incident photon energy.

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Inelastic scattering of x rays at energies in the vicinity of a deep-core–electron binding energy has attracted recent experimental and theoretical attention. The scattering of a characteristic x-ray line from targets of various elements whose K binding energies lie near the x-ray photon energy has been observed by Sparks[1] and investigated more recently by Suortti.[2] Eisenberger, Platzman, and Winick,[3,4] using the powerful technique of tunable synchrotron radiation excitation, have studied resonant x-ray inelastic scattering as the incident photon energy was varied in the vicinity of the K edge of copper in a metallic target.

The observed inelastic scattering is attributed to both the $\vec{p}\cdot\vec{A}$ term in second order and the A^2 term in first order of perturbation theory in the Hamiltonian describing the interaction of electrons and the radiation field. In the vicinity of an absorption discontinuity, the $\vec{p}\cdot\vec{A}$ contribution in second order exhibits a resonant character which dominates the usual Compton scattering by free electrons which is described by the A^2 term.

Inelastic scattering of x rays by bound electrons is accompanied by either an excitation of a core electron into the continuum, or, by excitation of the core electron into a bound excited state of the system. According to Sommerfeld,[5] the former possibility, which results in a continuous photon band with a definite limit on the high-energy side, is ascribed to Compton scattering of bound electrons, while the latter results in discrete inelastically scattered photon lines which are classed as Raman lines. Thus whether or not inelastic x-ray scattering of bound electrons in the vicinity of an absorption discontinuity is called Compton or Raman scattering depends on the final state of the core electron.

In this paper, we present the first observation of resonant x-ray Raman scattering in the vicinity of a discrete inner level of a quasiatomic system. Furthermore, the high-resolution inelastically scattered photon spectra obtained allow us to identify explicitly the contributions due to Compton and Raman lines and to study their behavior as a function of incident photon energy.

Figure 1 shows the two possible final states of the atomic system and radiation field in resonant x-ray scattering described by the $\vec{p}\cdot\vec{A}$ term in second order. In all experiments reported to date, inelastic x-ray scattering from metals at photon energies near the binding energy of a deep core level has been investigated. The resonant character of the process in these cases is evident only at photon energies below the core-electron binding energy, and the inelastically scattered radiation cannot be separated from the fluorescence radiation at photon energies close to, but above, the core-electron binding energy.

In the present experiment, we investigated inelastic x-ray scattering at photon energies in the vicinity of the white line in the manganese K absorption spectrum in $KMnO_4$. The large peak, observed in many K- and L-edge absorption coefficients near the absorption discontinuity, and known as a "white line," is generally ascribed to density of final states or excitonic effects. The white line in the manganese K absorption spectrum of $KMnO_4$ is interpreted[6] as being due to an excitation of a manganese $1s$ electron to a $3t_2$ molecular orbital of the $(MnO_4)^-$ ion. This bound level has a predominantly atomic manganese $4p$ character. By varying the incident photon energy in the vicinity of the white line or "$(1s)^{-1}(4p)^{+1}$" excitation energy, discrete resonant Raman lines can be investigated and their resonant nature studied below and above the resonance energy (Fig. 1).

The experimental arrangement was as follows: Synchrotron radiation from the DCI storage ring at Laboratoire d' Utilisation du Rayonnement Electromagnétique was monochromatized by a Si(220) channel cut crystal. The monochromatized beam of 10^9 photons/sec in a 2.2 eV bandwidth at 6.5 keV impinged on a pressed powder target of $KMnO_4$.

The fluorescent and scattered radiations were analyzed with a Johann geometry Ge(111) curved crystal of 50 cm radius, and the spectrum recorded with a "backgammon" position-sensitive counter.[7] This arrangement enabled us to record an 80 eV energy span in the vicinity of the manganese $K\alpha$ fluorescence lines with an instrumental

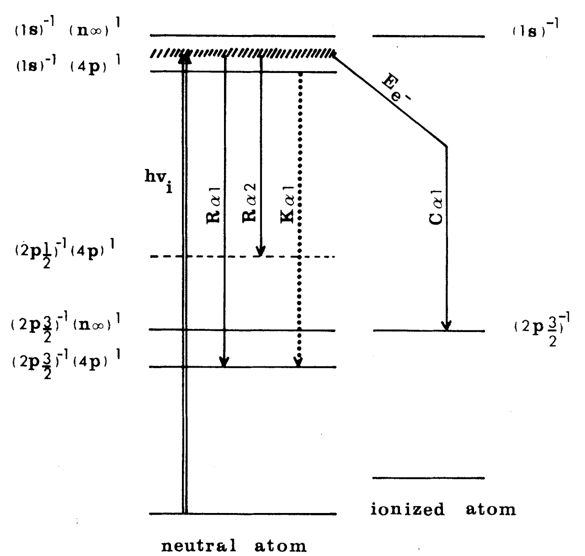

FIG. 1. Schematic representation of Raman and Compton scattering: $R\alpha_1$ and $R\alpha_2$ refer to Raman scattering of a photon of energy $h\nu_i$ resulting in a vacancy in the L_{II} or L_{III} subshell and an electron in a bound state of the system; $K\alpha_1$ refers to the characteristic K-L_{III} x-ray; $C\alpha_1$ refers to the radiative part of the Compton effect resulting in a vacancy in the L_{III} subshell of the ionized atom (E_e is the corresponding energy of the ejected Compton electron). For simplicity, $C\alpha_2$ has not been drawn.

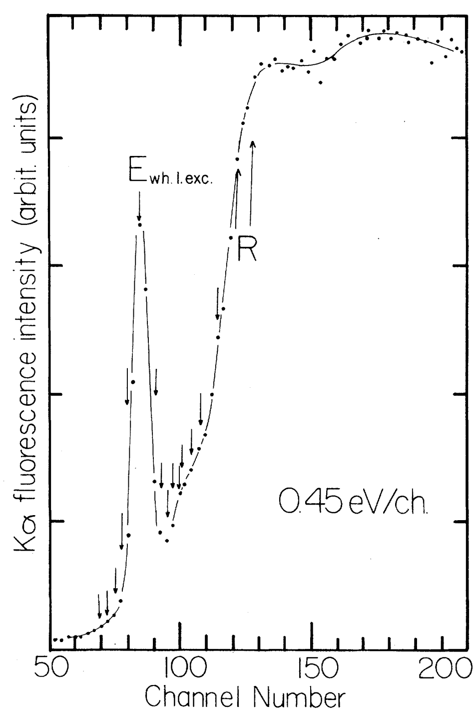

FIG. 2. Manganese K absorption spectrum of $KMnO_4$. Incident photon energies at which high-resolution inelastically scattered x-ray spectra were recorded are indicated by arrows. Reference $K\alpha$ fluorescence recorded at R.

resolution of 0.33 eV.

The K absorption spectrum of manganese in $KMnO_4$ was obtained by recording the K fluorescence radiation with a Si(Li) solid-state detector as a function of incident photon excitation energy and is shown in Fig. 2. Figures 3(a) and 3(b) show the high-resolution inelastically scattered x-ray spectra (after subtraction of observed $K\alpha$ x rays which arise from different effects, and which provided a convenient energy calibration reference) observed at photon excitation energies 8 eV below and 3.57 eV above the white line of $KMnO_4$.

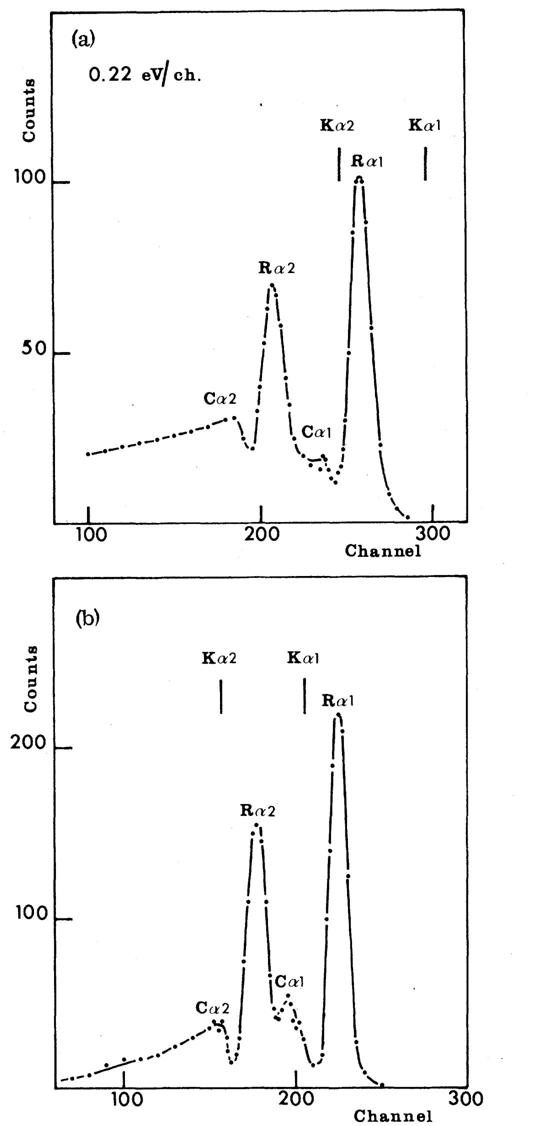

FIG. 3. Resulting Raman ($R\alpha_1$ and $R\alpha_2$) and Compton ($C\alpha_1$ and $C\alpha_2$) spectrum after $K\alpha_1$, $K\alpha_2$ x-ray subtraction at two different incident photon energies: (a) $E_{\text{incident}} - E_{\text{white line exc.}} = -8$ eV; (b) $E_{\text{incident}} - E_{\text{white line exc.}} = +3.6$ eV. Note the fast evolution of the Compton shape.

The energies of the discrete (Raman) lines have been found to exhibit the expected linear dependence on incoming photon energy (both above and below the white line excitation energy). The resonant nature of the Raman scattering is clearly evident in Fig. 4 in which the intensity of one of the Raman lines, $R\alpha_1$ (scattering accompanied by L_3 electron excitation), is plotted as a function of incident photon energy. The width and shape of the Raman lines were found to be related to the width and shape of the excitation line, an observation in agreement with Eisenberger, Platzman, and Winick.[3] No appreciable increase in Raman scattering was observed beyond the $(1s)^{-1}$-$(4p)^{+1}$ excitation energy, indicating that the major contribution to Raman scattering is due to the $4p$ level.

As shown in Fig. 3, and in each spectrum recorded, we have observed, in addition to the discrete Raman lines, broad continua whose max-

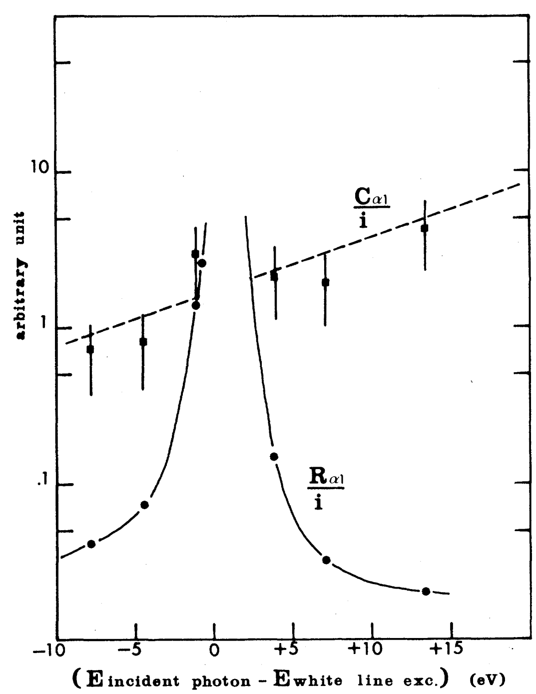

FIG. 4. Observed Raman ($R\alpha_1$) and Compton ($C\alpha_1$) intensity (corrected for same counting time interval and storage-ring electron beam intensity) vs incident photon energy. Error bars associated with the Compton intensity account for the small observed fraction of the whole spectrum whose shape is not known. The lines drawn through the points are to guide the eye only.

imum energy is always located at ~10 eV below the Raman peaks. These continua have been interpreted as due to Compton scattering of core electrons, i.e., inelastic scattering accompanied by ejection of an L electron into the continuum. (The constant energy difference between the Raman line R and maximum energy C of the Compton continuum being of the order of the energy difference between the $4p$ level and the ionization limit.) The shape of these continua varies, becoming sharper as the excitation energy is increased [Figs. 3(a) and 3(b)], in agreement with observations by Sparks[1] and Gavrila.[8]

Since the shape of the Compton continua is not well known and varies with excitation energy, deconvolution of the spectra is difficult, particularly in the vicinity of the white line excitation energy. We have nevertheless made a rough determination of the total Compton continua intensity as a function of incident photon energy. The results are shown in Fig. 4 together with the intensity variation of one of the Raman lines. As shown, the behavior of both processes, Raman and Compton, as a function of incident photon energy is unambiguously different. Raman scattering, dominant in the vicinity of the white line excitation energy, clearly exhibits a resonant character, while Compton scattering of bound electrons exhibits a smooth variation in intensity as the nearby ionization threshold is approached.

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