Inelastic Resonance Emission of X Rays: Anomalous Scattering Associated with Anomalous Dispersion*

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(Received 13 May 1974)

An inelastic resonance scattering of monochromatic Cu $K\alpha$ x rays incident on various targets is observed when an absorption edge of the target is just above the energy of the incident x rays. This frequency-dependent and angular-independent inelastic scattering is interpreted with the x-ray scattering theory of anomalous dispersion. Conservation-of-intensity arguments allow a comparison of the observed inelastic intensity with the real part of the anomalous dispersion corrections to the coherent atomic scattering factors for x rays.

I have observed a kind of inelastic x-ray scattering process that differs from the previously reported Compton and more recently described Compton-Raman[1,2] inelastic scattering. The inelastically scattered radiation was found when a Si(Li) detector was used for energy analysis of the x rays scattered from targets on which monochromatic Cu $K\alpha$ or Mo $K\alpha$ x rays impinged. As the incident radiation approaches an absorption edge of the target element, the inelastic scattering increases rapidly in intensity. The cross section for the observed scattering is shown to be predicted by the $\vec{P}\cdot\vec{A}$ term in second-order perturbation theory, a term previously neglected in inelastic x-ray scattering calculations.

An experiment similar to our diffuse-x-ray experiments[3] was constructed to measure the radiation given off by elements irradiated by a source of Cu $K\alpha$ or Mo $K\alpha$ x rays monochromatized by diffraction from the basal planes of highly oriented graphite.[4] This arrangement is shown in Fig. 1(a). The angle of the incident (exciting) radiation was equal to the angle of the detected radiation with respect to the specimen surface, so that the absorption path length is independent of scattering angle φ for thick samples. An ORTEC Si(Li) detector, with 190-eV resolution at 5.9 keV, associated electronics, and a multichannel analyzer were used to record the energy spec-

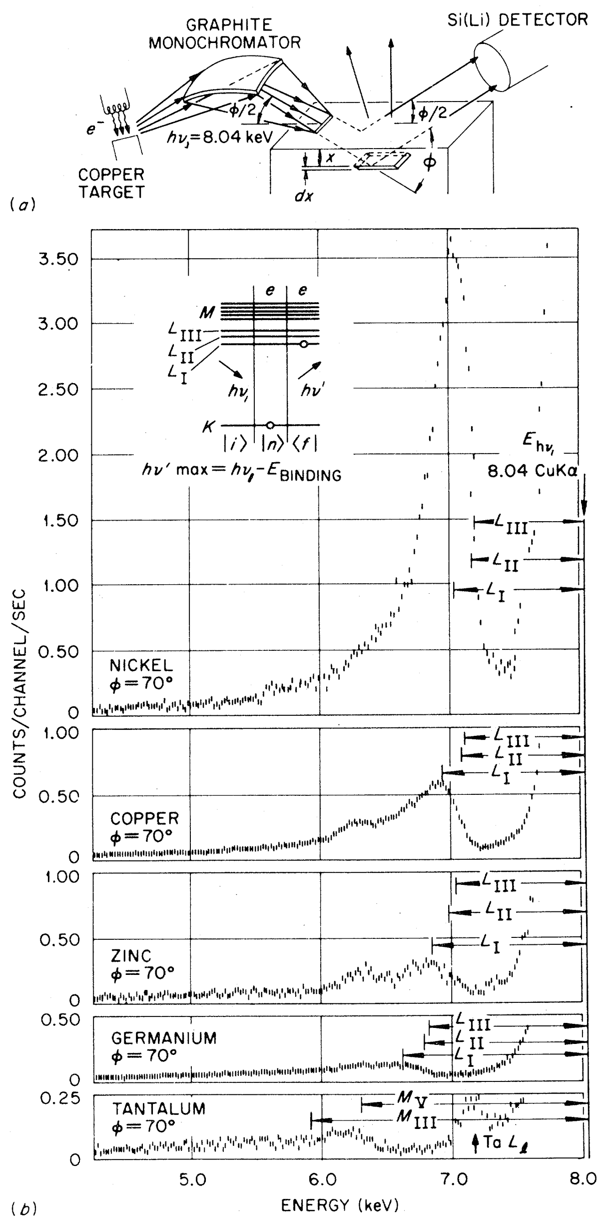

FIG. 1. (a) The experimental arrangement for the monochromatization of the incident x rays and detection of the scattered radiation. (b) Energy distribution of anomalous scattered x rays from elements irradiated with Cu $K\alpha$ x rays. Upper left inset shows the proposed quantum mechanism for the anomalous scattering; the electron hole may be in any of the three L-shell sublevels. The transitions may occur between any inner and outer shell.

trum of the radiation from various elements and their combinations. Figure 1(b) gives the results for a few elements. The main intensity maximum at 8.04 keV is due to the incident Cu $K\alpha$ x rays scattered from the specimen by Bragg scattering, thermal motion, and Compton scattering. The Compton shift is not large enough to be resolved by this detector. Lower-energy photons peaked in intensity at an energy E_s equal to that of the incident photon minus the binding energy of the most tightly bound electron shell from which electrons could be ejected by the 8.04-keV x rays. Although the spectra plotted were measured at $\varphi = 70°$, the intensity is isotropic, being independent of angle for the angles $10 \leq \varphi \leq 140°$ permitted by the experimental arrangement. Measurements were also made with monochromatic Mo $K\alpha$ x rays incident on various elements with similar results. A small part of the incident beam (subharmonics passed by the monochromator) accounts for the Ta L_1 fluorescent radiation in Fig. 1(b). Diagrammed at the upper left of Fig. 1(b) are the transitions from the initial ground state of the atom, $|i\rangle$, to the intermediate virtual state $|n\rangle$, and then to the final state $\langle f|$ where the atom is left with a hole in the L shell, and an x ray of energy $h\nu'$ has been emitted.

To facilitate the comparison of this observed inelastic radiation with theoretical predictions, I converted the measured intensity into absolute units following the procedure given in Ref. 3. A standard unit is the scattering by a free classical electron as calculated by Thomson.[5] I have assumed that the inelastic scattering is unpolarized since the intensity is angular independent in its spatial distribution.

Data such as in Fig. 1(b) were corrected for background, for the small Si escape peak generated in the Si(Li) solid-state detector, and for absorption in the sample. The corrected intensity was then integrated from 4.8 keV (background on the low-energy side) to the minimum just at the high-energy side of the inelastic spectrum. These results in electron units per atom are given in Table I with the theoretical values of the Compton-scattered intensity for comparison.

X-ray satellites on the high-energy side of primary (characteristic) x-ray spectral lines have been observed since the early days of x rays and are accounted for by multiple ionization of inner shells. More recently, satellites on the low-energy side of characteristic lines have been reported and attributed to a semi-Auger effect.[6] Lower-energy lines such as the early observations by Das Gupta[1] and more recently by Suzuki *et al.*[2] have been attributed to a Compton-Raman type of scatter in which a bound electron recoils with just enough energy to be ejected, leaving the photon reduced in energy by the binding energy of this ejected K electron. The latter observation on low-Z materials reports the intensity to be angular dependent.

Perturbation theory[7] is normally used to describe electron-photon interactions in problems

TABLE I. Cross sections in electron units per atom for the observed anomalous spectrum excited with Cu $K\alpha$ radiation. Compton scattering cross sections and theoretical predictions are given for comparison.

Element	φ (deg)	Compton[a] (e.u./atom)	Anomalous scattering Obs. (e.u./atom)	Anomalous scattering Calc. (e.u./atom)
Ni	30	4.88	7.0 ± 0.2	6.74
	90	12.14		
Cu	30	4.47	2.5 ± 0.4	3.4
	90	12.06		
Zn	30	4.61	1.3 ± 0.5	2.3
	90	12.21		
Ge	30	5.23	1.1 ± 0.4	1.6
	90	12.64		
Ta	30	8.18	7.0 ± 1.5	5.3
	90	21.43		

[a]D. T. Cromer, J. Chem. Phys. 50, 4857 (1969); D. T. Cromer and J. B. Mann, *ibid.* 47, 1892 (1967).

of this kind. The perturbation is the interaction Hamiltonian

$$\Delta V = e^2A^2/2mc^2 - e\vec{P}\cdot\vec{A}/mc, \qquad (1)$$

where $\vec{P}$ is the electron momentum, and $\vec{A}$ is the vector potential for the electromagnetic field. The Compton-Raman[1,2] observation was reportedly explained[8] by the two-photon process which arises from applying first-order perturbation theory to the A^2 term in ΔV and which predicts a frequency-independent cross section for the nominal 10-keV x rays used.

To explain my observations, I chose to look at the $\vec{P}\cdot\vec{A}$ term in second-order perturbation theory[7] for the following reasons: This term gives the observed angular independence for the intensity, and the energy denominators are small when the incident frequency approaches an absorption edge, giving the observed frequency dependence. This term has been used in the theory of anomalous dispersion, giving the factors $\Delta f'$ (real) and $\Delta f''$ (imaginary) which are the frequency-dependent but angular-independent corrections to the coherent atomic scattering factors.[9] The term $\Delta f'$ is often referred to as the Hönl correction. With these corrections for dispersion, the coherent x-ray atomic scattering factor is written as

$$f' = f_0 + \Delta f' + i\Delta f'', \qquad (2)$$

where f_0 is the usual coherent atomic scattering factor uncorrected for frequency dependence (dispersion). Coherent scattering (no change in incident x-ray frequency) occurs when the final state of the atom, $\langle f|$, is the same as the initial state $\langle i|$.[5,7] If $\Delta f'$ is negative, some of the coherent scattering events, represented by the atomic scattering amplitude f_0 calculated from the A^2 term in first-order perturbation theory, do not take place. To conserve energy or intensity, we need to account for those photons associated with the negative amplitude $\Delta f'$. These inelastic events are contained in the solution to the $\vec{P}\cdot\vec{A}$ term in second order for $\langle f| \neq \langle i|$.

There is a similar analogy to this argument for the coherent and Compton (incoherent) scattering cross sections calculated from the A^2 term. The coherent scattering amplitude f_0 is calculated from the A^2 term with $\langle f| = \langle i|$, but the Compton scattering is calculated from the A^2 term with $\langle f| \neq \langle i|$. For forward scattering, f_0 equals Z, the number of electrons in the atom. As the scattering angle increases, f_0 decreases, but the Compton cross section increases in such a manner that intensity tends to be conserved for each electron when all final states of the atom are considered for the A^2 term. This result, discussed by James,[5] is assumed to hold for the $\vec{P}\cdot\vec{A}$ term in second order, as this calculation for the condition $\langle f| \neq \langle i|$ has not been made for x-ray scattering. However, we may test the possibility that the amplitude of the inelastically scattered x rays observed in my experiment may be due to those lost from the coherent process with amplitude $\Delta f'$ by using the results obtained from the wave-mechanical treatment for oscillators as reviewed by James.[5]

As the observed intensity is incoherent, we may sum the scattering from each electron. Negative values contributed to $\Delta f'$ by the individual electrons will be taken as contributions to the incoherent scattering process. As $\Delta f''$ always makes a positive contribution to the coherent scattering, it cannot contribute to the inelastic anomalous scattering.

To calculate the intensity, we define an anomalous scattering amplitude factor per k electron, f_k^A, as

$$f_k^A = \Delta f'/n_k, \qquad (3)$$

where the subscript k denotes the electron shell or subshell and n_k the number of electrons in it. The division by n_k to obtain f_k^A is required as listings of $\Delta f_k'$ include all the electrons in the kth level. The intensity in electron units per atom is obtained by squaring the amplitude for each electron and then summing the intensity from each electron in the atom according to the following formula:

$$I/N = \sum_k |f_k^A|^2 = \sum_k |\Delta f_k'/n_k|^2, \qquad (4)$$

where the anomalous scattering amplitude $\Delta f_k'$ for the kth shell is in units of the Thomson scattering, and the sum is over those electrons in the energy levels that are in near resonance with the incident energy.

The real part of the anomalous scattering amplitude is given by James[5] (Eq. 4.30a, p. 145) as

$$\Delta f' = \sum_k \int_{\nu_k}^{\infty} \frac{\nu^2 (dg/d\nu)_k}{\nu_i^2 - \nu^2}\, d\nu, \qquad (5)$$

where ν is the variable of integration, ν_k and ν_i the frequencies of the absorption edge and the incident radiation, respectively, and $(dg/d\nu)_k$ the oscillator density at ν. Following the earlier work of Wheeler and Bearden,[10] Cromer[11] applied the concept of the sum rule to calculate the oscillator strengths without making the extrapolation over the continuum of the hydrogenlike atom. Cromer's oscillator strengths were used with the calculations given by Parratt and Hempstead[12] for the frequency-dependent part of the integral of Eq. (5) to determine the contribution of the kth-shell electrons to $\Delta f_k'$. The contributions from the K shell dominated my results except for the case of Ta where the L shell makes the major contribution when the incident radiation is Cu $K\alpha$. These values of $\Delta f_k'$ were then used to compute the incoherent intensity from Eq. (4). Results from these calculations are listed in Table I for comparison with the observed incoherent intensity, listed with an estimate of the error based on the counting statistics.

I was unable to observe the anomalous scatter shifted by the binding energy of the M shell for elements of Z around 30 since the detector could not resolve the approximately 100-eV energy shift from the incident energy. As my measurements did not include this inelastic scatter or energies below 4.8 keV, the observed values are expected to be less than those predicted by my calculation.

The virtual transition of the electron to a higher-energy state in an attempt to scatter coherently may result in the ejection of an electron from the atom. The kinetic energy with which the electron leaves the atom accounts for the energy distribution on the low-energy side of the anomalous spectrum. Electron spectroscopy[13,14] supports this view with observations that electrons leave the atom with little or no kinetic energy, often referred to as "electron shakeoff."

An experiment reported by Åberg and Utriainen[6] showed a broad x-ray spectrum on the low-energy side of the $K\alpha$ line with a long, low-energy tail as observed here. It is difficult to say if their weak spectrum, excited by raw Cr target x rays, arise from the initial K-electron vacancy being filled by a radiative Auger effect as they have interpreted it, or whether it arises from the large amount of fluorescent $K\alpha$ radiation produced in their sample which is in near resonance with its own K absorption edge. This latter explanation based on the work reported here fits their gross observations well.

The author would like to thank J. S. Faulkner for help in the quantum mechanical theory and encouragement in this study, J. Korringa for interpreting my understanding of the quantum analog, H. C. Schweinler for sharing his helpful insights concerning oscillator strengths, and B. S. Borie and H. L. Yakel for corrections and comments on the manuscript.

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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