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Brief Reports

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X-ray parametric scattering from atomic *K*-shell electrons

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We have calculated the scattering cross section for a third-order process in which a hard x ray incident on an atomic system is absorbed with the emission of two lower-energy x rays. This process is resonant when one of the two lower-energy x rays has an energy equal to the *K*-shell binding energy. We calculated the resonant term in the scattering with a one-electron model using shielded hydrogenic wave functions. This work was motivated by a recent coincidence inelastic x-ray scattering experiment on copper which claimed to show by such scattering. We find that even at resonance the third-order scattering process is too weak by 3 orders of magnitude to account for the spectral feature which was attributed to it.

I. INTRODUCTION

Parametric scattering is a process in which a photon is absorbed with the emission of two photons of lower energy which add up to the incident energy. It has been observed in both the optical and x-ray regions. In the optical region the effect is inhibited by the dipole selection rules for optical absorption and emission and the effect is only seen in systems which lack a center of symmetry.[1] In these systems the electron wave functions do not have a definite parity and dipole transitions can take the system from the initial state though two intermediate states and back to the initial state. In the x-ray region the wavelengths are short enough that absorption and emission can proceed though radiation moments higher than the dipole, and the requirement that the system lack a center of symmetry is dropped. A further requirement is that of spatial phase coherence of the electromagnetic field, which microscopically is the conservation of momentum for photons. The conservation laws for scattering in which photon 1 is absorbed with the emission of photons 2 and 3 are

$$\omega_1=\omega_2+\omega_3 ,$$

$$\mathbf{k}_1=\mathbf{k}_2+\mathbf{k}_3 .$$

In free space, where $\omega=c\,|\,\mathbf{k}\,|$, this condition can be satisfied only if $\mathbf{k}_2$ and $\mathbf{k}_3$ are collinear with each other and with $\mathbf{k}_1$. In the optical region a nonuniform dispersion relation $\omega=c\,|\,\mathbf{k}\,|/n(\mathbf{k},\epsilon)$ can break this constraint. In the x-ray region the constraint can be broken by performing the scattering in an inhomogeneous medium in which momentum is not conserved, such as a crystal. There the phase coherence condition becomes $\mathbf{k}_1=\mathbf{k}_2+\mathbf{k}_3+\mathbf{G}$, where $\mathbf{G}$ is a crystal-lattice vector. In this case there are conditions for parametric scattering in crystals analogous to those for Bragg scattering. A third way to meet the momentum constraint is to directly transfer photon momentum to the system. In this case a third particle such as an electron carries off momentum. The theory of x-ray parametric scattering of Freund and Levine[2] was used by Eisenberger and McCall to explain their observation of the effect with molybdenum $K\alpha$ x rays (17 keV) incident on crystalline beryllium.[3] They also showed that the approximations used by Freund and Levine were essentially equivalent to treating the scattering classically as a nonlinear mixing of two electromagnetic fields by a free classical charge. The approximations made were that the x-ray energies were both much greater than electronic binding energies and much smaller than the electron mass. We have made a calculation of the scattering cross section in which atomic binding effects are important. The system of interest is an x-ray scattering from a *K*-shell electron. In particular, we studied a resonant process in which one x ray is emitted with an energy comparable to the *K*-shell binding energy. We used a one-electron model with hydrogenic wave functions and second-order perturbation theory with the nonrelativistic scattering Hamiltonian. The effect of other electrons was to restrict the available intermediate states and to set the lifetimes of the intermediate states.

II. PREVIOUS MOTIVATING EXPERIMENT

An experiment sensitive to the detection of atomic x-ray parametric scattering was performed by Namikawa and Hosoya.[4] In it 59.6-keV x rays from an ^{241}Am radioactive source were incident upon a copper-foil target. Two solid-state detectors viewed the target. The output of one was analyzed with a single-channel analyzer set to a window enclosing the copper K fluorescence lines. The output from the single-channel analyzer along with coincidence detection circuitry was used to gate the output of the second detector, which was recorded with a pulse-height analyzer. This system recorded Compton scattering from K-shell electrons in which the electron is ejected from the K shell and the core hole relaxed with the emission of a fluorescence x ray. It was also sensitive to parametric scattering events in which one of the two emitted photons had an energy near the fluorescence line energy. The two photons emitted in a parametric scattering event must have a total energy equal to the incident energy. If one of these photons lies in the energy window around the fluorescence energy the other will have an energy just above the K edge in the scattering spectrum.

III. CROSS-SECTION CALCULATION

We calculated the cross section for a third-order scattering in which an incident x ray with energy ω_1, momentum $\mathbf{k}_1$, and polarization $\boldsymbol{\epsilon}_1$ is absorbed with the emission of two x rays of energies ω_2 and ω_3. The scattering was that calculated for the particular atomic process in which a K-shell electron is excited to a bound- or low-continuum state and then radiatively decays back to the K shell. We were interested in an energy region in which this process is resonant and we ignored interference terms with other scattering processes. The nonrelativistic Hamiltonian used to describe the scattering is

$$H=H_{\text{atom}}+\frac{1}{c}\mathbf{p}\cdot\mathbf{A}(\mathbf{r})+\frac{1}{2c^2}\,|\,\mathbf{A}(\mathbf{r})\,|^2\,.$$

In atomic units

$$\hbar=e^2=m_e=1,\quad c=137.03604\,.$$

The scattering cross section was calculated with second-order perturbation theory. The intermediate states were those with the electron in a bound or continuum state. The cross section is written

$$\frac{d\sigma}{d\omega_2 d\Omega_2 d\Omega_3}=\frac{2\pi}{c^6}\frac{k_2k_3}{(2\pi)^3k_1}\,|\,\boldsymbol{\epsilon}_1\cdot\boldsymbol{\epsilon}_2^*\,|^2\,|\,M_{DT}\,|^2 \qquad (1)$$

in which Ω_2 and Ω_3 are the solid angles into which the photons ω_2 and ω_3 are emitted. M_{DT} is an atomic matrix element,

$$M_{DT}=\int_\lambda\frac{(-i)\langle i\,|\,\boldsymbol{\epsilon}_3^*\cdot\mathbf{p}\,|\,\lambda\rangle\langle\lambda\,|\,e^{i\mathbf{Q}\cdot\mathbf{r}}\,|\,i\rangle}{\omega-(E_\lambda-E_i)+i\Gamma/2}\,, \qquad (2)$$

where $\omega=\omega_1-\omega_2$ and $\mathbf{Q}=\mathbf{k}_1-\mathbf{k}_2$. The parameter λ is either a radial quantum number of a bound state or the energy of a continuum state. The transition from the ground to the intermediate state is through the third term in the Hamiltonian and will result in the absorption of ω_1 and the emission of ω_2. The transition back to ground state is through the second term of the Hamiltonian. For the resonant process $\omega_3=E_\lambda-E_i$, which is approximately the energy of the $K\beta$ line. We used the dipole approximation for the transition from the intermediate state back to the initial state, so only intermediate states with $l=1$ had to be considered. We converted the $\boldsymbol{\epsilon}_3^*\cdot\mathbf{p}$ matrix element to the length form and summed over the $m_l=1,0,-1$ states and over the two independent polarizations for $\boldsymbol{\epsilon}_3$,

$$|\,M_{DT}\,|^2=\tfrac{2}{3}\sin^2\theta_Q\left|\int_\lambda\frac{(E_\lambda-E_i)I_1(\lambda)I_2(\lambda,Q)}{\omega-(E_\lambda-E_i)+i\Gamma/2}\right|^2. \qquad (3)$$

The integrals $I_1(\lambda)$ and $I_2(\lambda,Q)$ are radial integrals of the radial parts of atomic wave functions,

$$I_1(\lambda)=\int f_i(r)rf_\lambda(r)r^2dr\,, \qquad (4)$$

$$I_2(\lambda,Q)=\int f_i(r)j_1(Qr)f_\lambda(r)r^2dr\,. \qquad (5)$$

The functions $f_x(r)$ are the radial parts of the wave functions and θ_Q is the angle between $\mathbf{Q}$ and $\mathbf{k}_3$. Shielded hydrogenic wave functions[5] were used for initial and intermediate states. A different value of the effective nuclear charge was used for the initial and intermediate states, Z_i denoting the charge for the initial states and Z_λ that for the intermediate state.

The integrations over the radial wave functions using hydrogenic wave functions were performed analytically (see the Appendix). The sum over intermediate steps was done in two parts, a summation over discrete states followed by integration over a continuum. The first unoccupied p state in copper corresponds to $n=4$. The bound states up to $n=44$ were discretely summed. We then integrated numerically over the remaining discrete states and over the continuum states. The higher bound states were treated as part of the continuum and were normalized for integration over energy by multiplying each by the square root of the density of states $g(n)$ of the discrete states: $g(n)=n^3/Z_\lambda^2$. The numerical integration over the sharply peaked resonance was facilitated by changing to a different variable of integration ϕ, the phase of the resonance: $\phi=\arg[\omega-(E_\lambda-E_i)+i\Gamma/2]$.

IV. SELECTION OF PARAMETERS

The cross section was evaluated for the case of 59.6-keV x rays incident on a copper atom in order to simulate the experimental case. The parameter Γ is the width of the intermediate state and is related to the lifetime of the atomic state with a core electron excited to a bound or continuum orbital. We assumed that this lifetime is limited by the decay of the core hole through fluorescence and Auger electron emission and is independent of the intermediate state of the excited electron. The width was set to 3.20 eV. This value is the K x-ray linewidth for copper, obtained by interpolating between the experimental values of the K widths for nickel and zinc.[6] The parameter Z_λ is the shielded nuclear charge used for the intermediate-state wave function. We chose it by a method previously used for continuum shielded hydrogenic wave functions used in an Auger-process calculation.[7]

This method specifies that the shielded charge for an electron emitted from a $1s$ state is the geometric mean of the effective charges of the $1s$ and the $2s$ states. The effective charge for the $1s$ state is the unshielded nuclear charge $Z_{1s}=29$. The effective charge for the $2s$ state was calculated from the radial expectation value obtained in a relativistic Hartree-Fock calculation.[8] This procedure gave $Z_{2s}=25.6$ and consequently $Z_\lambda=27.25$. We also made several calculations to check the effect of changing these parameters on the strength of the scattering.

The geometry used in the calculation was that for the experiment cited, in which 59.6-keV x rays were scattered from copper through 135°. Another detector system set to give a gating signal for copper fluorescence x rays was set at an angle of 77° to the original photon direction. If the photon going to the detector at 135° is regarded as photon 2 then the momentum transfer $\mathbf{Q}$ is nearly perpendicular to the direction of $\mathbf{k}_3$ ($\theta_Q \approx 82°$). The angle θ_Q was therefore approximated to be 90° for all energies. The source was unpolarized, so $|\boldsymbol{\epsilon}_1\cdot\boldsymbol{\epsilon}_2^*|^2=0.75$ when summed over final states and averaged over initial polarizations. The cross section is also increased by a factor of 4 since the contributions from the two K-shell electrons contribute coherently to the matrix element.

V. RESULTS

Figure 1 shows the differential scattering cross section versus ω_2 for a scattering angle $\theta=135°$. An experiment in which only those events in which ω_3 falls in a specified energy window set by a single-channel analyzer corresponds to taking a slice in energy of the spectrum shown in Fig. 1. For comparison Fig. 1 also shows the spectrum obtained from Compton scattering off the K-shell electrons in the approximation where the electron final states are plane waves. In this case the third photon is a fluorescence x ray which is assumed to be emitted isotropically and with a probability equal to the fluorescence efficiency.[9]

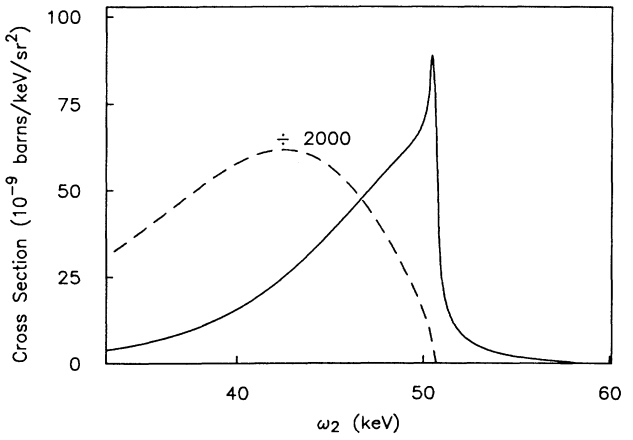

FIG. 1. Double differential scattering cross section for resonant parametric scattering (solid line). Evaluated for 59.6-keV x rays incident on copper at a scattering angle of 135° with instrumental broadening of 360 eV. Also plotted is the Compton scattering from copper K-shell electrons in the plane-wave final states approximation (dashed line). The height of the Compton spectrum has been reduced by a factor of 2000.

In order to check the dependence of the calculated results on the model parameters, particularly on the value of Z_λ, we did a number of calculations in which these parameters were varied. For each choice of model parameters we calculated the cross section integrated over a range of energies of ω_2. This number gives the total signal which would be seen in the experiment if the detection of the higher energy photon were gated by the simultaneous detection of the lower energy photon satisfying 7.0 keV $\leq \omega_3 \leq$ 10.0 keV. The results of these calculations appear in Table I. Over a range of reasonable values for the parameters Γ and Z_λ the result for this cross section varied by less than a factor of 2 from that obtained for the parameter values used in the calculation of the scattering spectrum (Fig. 1).

VI. CONCLUSIONS

The feature in the experimental spectrum which prompted this calculation was a shoulder seen in the spectrum of x rays scattered from Cu.[4] These scattered x rays were detected in coincidence with x rays falling in an energy window around the copper $K\alpha$ line. In terms of this calculation the experiment detected photon 2 when photon 3 satisfied the coincidence condition. The data does not suffice to establish an absolute experimental measurement of the cross section. However, the measured feature has approximately as much strength as the much wider feature attributed to Compton scattering from the two K-shell electrons. This calculation indicates that K-shell x ray parametric scattering, even at resonance, is down by over 3 orders of magnitude from the K-shell Compton scattering, and that the spectral feature cannot be a result of parametric scattering as reported. Solid-state effects should not be responsible for a great enhancement of this resonance. Any great increase in the density of states at the Fermi level would show up as a pronounced peak in copper photoabsorption spectra, and no such peak is seen.[10] In a recent comment[11] on this experiment Man-

TABLE I. Values of K-shell parametric scattering cross section $d^2\sigma/d\Omega_2 d\Omega_3$ for copper ($Z_i=29$) integrated from $\omega_3=7.0$ keV to $\omega_3=10.0$ keV for different values of model parameters Γ (intermediate-state width) and Z_λ (intermediate-state effective nuclear charge).

Z_λ	Γ (eV)	$d^2\sigma/d\Omega_2 d\Omega_3$ (10^{-8} barns/sr^2)
27.25	0.5	10.50
27.25	2.5	11.25
27.25	3.2	11.43
27.25	4.5	11.73
27.25	8.5	12.30
14	3.2	15.54
20	3.2	17.79
24	3.2	14.97
27.25	3.2	11.43
29	3.2	9.45
32	3.2	6.39

ninen has suggested that this and other spectral features near the K edge are the result of accidental coincidences.

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APPENDIX: INTEGRALS OF HYDROGENIC WAVE FUNCTIONS

The radial hydrogenic wave functions used in these calculations were[5]

$$f_i(r)=C_i e^{-Z_i r},\quad C_i=2Z_i^{3/2},$$

$$f_n(r)=C_n\frac{2Z_\lambda r}{n}e^{-Z_\lambda r/n}\,{}_1F_1(-n+2,4,-Z_\lambda r/n),$$

$$C_n=\frac{1}{6}\left[\frac{n^2-1}{2}\right]^{1/2}\left[\frac{2Z_\lambda}{n}\right]^{3/2},$$

$$f_E(r)=C_E(2kr)e^{-ikr}\,{}_1F_1(in'+2,4,2ikr),$$

$$C_E=\frac{(1+n'^2)^{1/2}}{3}\left[\frac{Z_\lambda}{1-e^{-2\pi n'}}\right]^{1/2},$$

where $k=(2E)^{1/2}$, $n'=Z_\lambda/k$.

f_i is the ground $1s$ state, while f_n and f_E are p states.

The integrations in Eqs. (A1) and (A2) were performed analytically,

$$I_1(n)=\left[\frac{2Z_\lambda}{n}\right]\frac{6C_iC_n(4Z_i-2Z_\lambda)}{(Z_i^2-k^2)^3}\left[\frac{Z_i-k}{Z_i+k}\right]^n$$

where $k=Z_\lambda/n$, (A1a)

$$I_1(E)=2k\frac{6C_iC_E(4Z_i-2Z_\lambda)}{(Z_i^2+k^2)^3}\exp[-2n'\arctan(k/Z_i)]$$

where $k=(2E)^{1/2}$, $n'=Z_\lambda/k$, (A1b)

$$I_2(n,Q)=\frac{3C_iC_n}{k^2n(n^2-1)Q^2}\left[\frac{r_+}{r_-}\right]^n$$

$$\times\{(Z_i+Z_\lambda)[B\cos L+(A-1)\sin L]$$

$$+Q(A\cos L-B\sin L)\}\quad\text{where } k=Z_\lambda/n,$$

(A2a)

$$r_\pm=|Z_i\pm k+iQ|,\quad \phi_\pm=\arg(Z_i\pm k+iQ),$$

$$L=-n(\phi_+-\phi_-),\quad A=\frac{4nQ^2kZ_i}{r_+^2r_-^2},$$

$$B=\frac{2nkQ}{r_+^2r_-^2}(Z_i^2-k^2-Q^2),$$

$$I_2(E,Q)=\frac{3C_iC_E}{k^2n'(n'^2+1)Q^2}\exp[-n'(\phi_+-\phi_-)]$$

$$\times\{(Z_i+Z_\lambda)[B\cos L+(A-1)\sin L]$$

$$+Q(A\cos L-B\sin L)\}$$

where $k=(2E)^{1/2}$, $n'=Z_\lambda/k$, (A2b)

$$r_\pm=|Z_i+i(Q\pm k)|,\quad \phi_\pm=\arg[Z_i+i(Q\pm k)],$$

$$L=n'\ln(r_+/r_-),\quad A=\frac{4n'Q^2kZ_i}{r_+^2r_-^2},$$

$$B=\frac{2n'kQ}{r_+^2r_-^2}(Z_i^2+k^2-Q^2).$$

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