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ABSTRACT

Elastic scattering of photons from solid samples of Pb, Pt, and W were measured in order to investigate the limits within which scattering experiments can be described as being due to free atoms. The experiments were performed with photons of 22.1 keV from a x-ray tube and from an Am^{241} (59.54 keV) gamma source, providing a momentum transfer ranging from $x = 0.1$ to $x = 2.0\mathring{A}^{-1}$. It is shown that the low momentum transfer limit for the free atom approximation will depend on the scatterer, temperature, geometrical resolution and on the accuracy of the experiment.

INTRODUCTION

Measurements of elastic scattering of photons by bound atomic electrons , known as Rayleigh scattering, are an important test of methods to calculate scattering amplitudes. They are also important in measuring higher order scattering amplitudes such as Delbruck scattering in which the amplitude of the effect corresponds to a few percent of the Rayleigh one[1]. In the low energy range, near absorption edges, an accurate knowledge of the elastic scattering cross section is particularly important[2].

Up to now, several experiments with photon energies ranging from keV to MeV have been performed, most of them with metals as scatterers[3,4]. The extent to which theories agree with the experimental data is still not completely clear but the most sucessful theoretical approach is clearly the second order perturbation theory, as developed by Kissel and Pratt[3,4], mainly

for energies above 100 keV with a corresponding momentum transfer $x > 10\mathring{A}^{-1}$, where $x = E/12.4 * sin(\theta/2)$, E in keV and θ = scattering angle . The worst agreement is in the $x < 10\mathring{A}^{-1}$ momentum transfer range with deviations up to 30% [5].

In a former work[6] we have reported the occurence of diffraction peaks in photon scattering diferential cross sections for polycrystaline samples due to Bragg scattering, which was probably responsible for the discrepancies pointed in (5).

In this work we try to explain these discrepancies in the low momentum transfer range and also to establish low momentum transfer limits of validity of Rayleigh scattering theories in describing the process in solid samples.

Two sets of experiments were performed, with different photon energies and geometrical resolutions. The results are compared with free atom and diffraction theories.

THEORY

Results of Rayleigh scattering amplitudes in the free atom approximation (FAA) using second order perturbation theory generally show good agreement when compared with measurements using solid or liquid samples[3]. Within 10%, form factor theories could also be used to predict scattering amplitudes for x less than $10\mathring{A}^{-1}$. But within this range, the cooperative effects due to the aggregate state of the atoms in the sample may turn meaningless the direct comparison of experimental data with results of free atom theories. Even the lacking of periodicity in the atomic arrangement of amorphous solids, liquids or non-monoatomic gases does not avoid the conditioning of the elastic scattering.

In the studies of condensed matter structure, it is usual to suppose that the elastic scattering of photons by atomic electron is well described by the form factor approximation. Although not completly true, this will be assumed here in order to investigate the transition between the free atom and the structure scattering regimes.

Following Warren[7], the intensity of elastic scattered radiation (energy by unit area by unit time at a distance R of the scatterer) from non-crystalline or polycrystalline samples with randomly oriented grains , for small momentum transfer (where the form factor approximation are expected to be valid) is given in electron units by:

$$I_s = I_e \sum_m \sum_n f_m f_n e^{i\mathbf{K}(\mathbf{R_m}-\mathbf{R_n})} \quad (1)$$

$$I_e = r_0^2/R^2[(1+cos^2\theta)/2]$$

where:

I_e = Thomson scattering intensity at a distance R from the electron

I_0 = intensity of incident radiation

r_0 = classical electron radius

θ = scattering angle

f_m, f_n = atomic form factors

$\mathbf{R_m}$,($\mathbf{R_n}$) = position of the mth (n^{th}) atom in the cell

$\mathbf{K}= 4\pi x$ = momentum transfer

Thermal vibration causes small displacements of m atom from $\mathbf{R_m}$ to $\mathbf{R_m} + \mu_m$ where μ_m is the instantaneous displacement of the mth atom. For polycrystalline samples with cubic unit cell and one atom per cell (monoatomic), the intensity becomes

$$I_s = I_e f^2 \sum_m \sum_n e^{i\mathbf{K}(\mathbf{R_m}-\mathbf{R_n})} e^{i\mathbf{K}(\mu_m-\mu_n)} \quad (2)$$

The $e^{i\mathbf{k}(\mu_m-\mu_n)}$ term is the only time-dependent term in eq (2). Since measurements are carried over a long period of time compared with temperature induced oscillations, this term must be taken as a time average.

With the oversimplified hypothesis of independent vibration of the atoms, Debye theory predicts the scattered intensity to be

$$I_s = I_e f^2 N(1-e^{-2M}) + I_e f^2 e^{-2M} \sum_m \sum_n e^{2\mathbf{K}(\mathbf{R_m}-\mathbf{R_n})} \quad (3)$$

where

$$2M = 2B(K/4\pi)^2 = 2Bx^2 \quad (4)$$

e^{-2M} is the Debye factor and B the temperature factor.

The first term in eq(3) is the thermal diffuse scattering (TDS) intensity in the independent atomic vibration model. This term tends to $I_e N f^2$ for large values of x , i.e, to the free atom scattering intensity. The theory of coupled atomic vibrations (fonons) predicts that the TDS intensity scattered by a polycrystaline sample (with a cubic face centered (FCC) unit cell for example), does not increase monotonically with the momentum transfer but has maxima coincident with the reciprocal lattice points. The widths of such peaks are larger than the corresponding Bragg ones. Between the reciprocal lattice points the results of the fonon scattering theory tends to the Debye theory results, i.e., the scattering increases with x and with the atomic vibration amplitude.

The second term in equation (3) is responsible for the ordinary crystalline diffraction and decreases with x due to the form factor and due to e^{-2M}. For small vibration amplitudes, even for relatively large momentum transfer, but still in the context of the diffraction formalism, the e^{-2M} factor can become small enough in order for the diffraction to be important (table 1 shows B values for W, Pt and Pb [8] .

For the case of polycrystalline samples with grains in preferential orientation (the most common case for metals) or monocrystalline samples, the Bragg peaks can be detected even for large values of x. Elastic scattering measurements with good precision made with x-ray diffraction for small x has been reported by different authors[10-13]. For the incident beam direction, the real part of the x-ray elastic scattering amplitude for silicon has been measured by interferometric methods with an accuracy better than a few tenths of percent[13]. For directions others than the incident, measurements using x-ray diffraction methods (Pendellosung) were made with comparable precision but, in order to obtain accurated scattering amplitudes for the isolated atom it is necessary to know the crystalline structure precisely.

At higher energies the distance between the reciprocal lattice points will be smaller, which means more Bragg peaks in the acceptance angle. If the angular resolution of the scattering measurement is poor, the diffraction peaks will not be detected. The aimed accuracy of the results will determine the necessary minimum angular resolution. Obviously, large angular resolution and high intensity, simultaneously, is not easy to achieve. Synchrotron radiation

may be a solution for this problem.

EXPERIMENTAL PROCEDURE

1) 59.54 keV Experiments

The measurements with photons of 59.54 keV were performed in the Instituto de Física of the Universidade Federal do Rio de Janeiro. Laminated foils of W, Pt and Pb with thickness of 200, 120 and 150 μm respectively were used as scatterers. The photon source was a $200mCi$ Am^{241} gamma source from Amershan. Source and scatterer were placed in a vacuum tube in order to eliminate the scattering in the air . The detection system was a GeLi detector, conventional spectroscopic electronic and a multichannel analyser. Details of the apparatus are reported elsewhere[6].

The results are presented in number of scattered photons per unit time (N_{scatt}), corrected for attenuation N_{corr}. The relation with the cross section is given by:

$$N_{corr} = N_{scat}\frac{1}{F_{att}} = N_0 N_{at}\frac{d\sigma}{d\Omega}$$

$1/F_att$ = attenuation correction factor

$d\sigma/d\omega$ = differential cross section in cm^2

N_0 = number of incident photons per unit time

N_{at} = number of illuminated atoms per cm^2

for normal incidence (angle between incidence direction and sample surface $\theta_i = 90°$)

$$\frac{1}{F_{att}} = -\frac{(e^{-\mu a} - e^{-\mu a/\cos\theta})}{a\mu(1 - 1/\cos\theta)}$$

where

μ = total attenuation coefficient in cm^2/g

a = scatterer thickness in g/cm^2

θ = scattering angle

The angular resolution was 0.3^0 for $\theta < 20^0$ and 0.5^0 for $\theta > 20^0$ resulting in a momentum transfer resolution Δx of about 0.02 $\mathring{A}^{-1}$.

2) 22.1 keV ($\kappa\alpha 1 = 22.16$, $\kappa\alpha 2 = 21.99$) experiment

The measurements with 22.1 keV photons were performed in the Departamento de Física. of the Universidade Federal do Parana, using the characteristic Ag $\kappa\alpha$ line from a x-ray tube in a conventional Bragg-Bretano focusing powder diffractometer with divergent and scattering slits equal to 2^0 and receiving slits of 0.3 mm. The same scatterers from the gamma experiment were measured using a scintillation NaI detector with a single channel analyser. For some scattering angles, the photon energy spectrum was measured with a GeHP detector in order to compare the measured elastic area with the corresponding one obtained with the NaI detector.

The lower energy resolution of the NaI did not worsen the resulting data error because, for this energy, the Compton intensity is not comparable with the elastic one, being of about 1% for the worst case (W, $x = 2.0\mathring{A}^{-1}$)

It was not necessary to correct the measured number of scattered photons for absorption since at this energy and angular range the sample thickness can be supposed infinite ($e^{-\mu t} = 10^{-7}$), which implies the same correction factor for all measured angles.

The angular resolution of the system was 0.1 degree, resulting in a momentum transfer resolution of 0.002 $\mathring{A}^{-1}$. It should be noted that in spite of the poorer resolution $\Delta E/E$ of the X-ray line (10^{-4}) when compared with the gamma line (10^{-6}), the resulting momentum transfer resolution in the x-ray case is 10 times better.

RESULTS AND CONCLUSIONS

Experimental results with theoretical predictions are shown in fig 1 to 3, all of them normalized to 1.

The curves labeled (a) are results of calculations of diffraction intensities considering reduction of the diffraction peaks due to TDS but not the resulting TDS intensities. The figures labeled (b) and (c) are the experimental results obtained with photons of 22.1 and 59.54 keV respectively. The solid line in fig.(c) is just a guide to the eye. The curves (d) are the theoretical predictions calculated for the free atom case with the modified form factor theory[9].

Figures (d) show the well known theoretical result that no oscilation is predicted by the free atom model. Figs (a) shows that even for $x > 1\mathring{A}^{-1}$, diffraction peaks can be expected. Due to TDS, some of them are concealed in the experimental curves (b), more for Pb and less for Pt and W . In the experiment done with γ rays (figures (c)) no peaks are detected at $x > 1\mathring{A}^{-1}$ not only due to TDS but also due to the lower x accuracy when comparing with the x-rays experiments.

Comparing figs (a) and (b) it is possible to see, for the Pt and W cases, the effect of preferential grain orientation. In fig 2 (Pt), the effect results in a reduction of the measured (hhh) peaks and in a increasing of the (h00) peaks. In fig 3 (W), the preferential grain orientation results in a reduction of (hh0) peaks and in a increasing of (h00) peaks, both pointed with arrows in fig 3a.

The use of form factor approximation instead perturbation theory does not change the conclusions, since the difference between both results in this momentum transfer range does not change the smoothness of the theoretical results.

Table I shows clearly the dependence of the scattered intensities on the sample and on the temperature. For W (the smallest B), the diffracted intensity will be reduced by TDS to 1% of the corresponding intensity without considering thermal oscilations for $x = 3.4\mathring{A}^{-1}$ at T=273 K and for $x = 6.8\mathring{A}^{-1}$ at T=0 K. For lead, the same condition will be reached for much smaller values of x: $x = 0.96\mathring{A}^{-1}$ at T=273 K and $x = 3.7\mathring{A}^{-1}$ at T=0 K.

In brief, six parameters are involved on Rayleigh scattering measurements: chemical element, atomic structure of the sample, temperature, moment transfer, angular resolution and the measurement accuracy. For a given sample, temperature and moment transfer, the detection of solid state effects like diffraction peaks depends on the angular resolution and on the measurement accuracy. It is convenient to divide momentum transfer in three regions without well defined limits, small ($x < 1\mathring{A}^{-1}$), medium ($1\mathring{A}^{-1} < x < 10\mathring{A}^{-1}$) and large ($x > 10\mathring{A}^{-1}$). For large x the hypothesis of free atom is valid for any chemical element, independent of the type of sample and temperature. For medium x the problem must be carefully analysed . For small values of x the solid state effects can not be ignored unless in exceptional cases like measurements of samples with large temperature factors B, at high

temperatures and in experiments with not very high accuracy.

It is easy to conclude that the lower momentum transfer limit of validity of free atom theories to explain the elastic scattering of photons by solid samples depends on the sample, the geometrical resolution of the experiment and on the temperature. Moreover, this limit for the studied elements lies between 0.5 and 2 $\mathring{A}^{-1}$. Comparision between experimental data and Rayleigh theories near this momentum transfers limits should be done only after a careful investigation to test the occurence of interference effects.

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FIGURE CAPTIONS

FIG 1. Results for Pb: a) Theoretical Bragg scattering intensities corrected for thermal vibrations. b) scattering intensities measured in a powder diffractometer using the Ag$\kappa\alpha$ line (E= 22.1 keV) - c) differential scattering cross sections measured with 59.56 keV photons from an Am^{241} γ source - d) theoretical differential cross sections ($d\sigma/d\omega$) obtained with form-factor theory[9].

FIG 2. The same as FIG 1 for Pt.

FIG 3. The same as FIG 1 for W. Some of the small peaks in fig. (b) which do not appear in fig. (a) are due to the unfiltered $Ag\kappa\beta$ radiation. Peaks modified by preferential grain orientation are pointed with arrows.

TABLE 1. Theoretical x values for which Bragg diffraction intensities are reduced to 0.1, 1 and 5 % of the intensity diffracted by a cristalline lattice without vibrations, for temperature 0 and 273 K. Values of B are an average of the values published by ITXRCr[7]

Table I

Temperature	Element	Deby Thermal Parameter (B)	x Value in A^{-1}		
			0.1%	1.0%	5.0%
0 K	Pb	.17	4.5	3.7	3.0
	Pt	.06	7.6	6.2	5.0
	W	.05	8.3	6.8	5.5
293 K	Pb	2.5	1.2	.96	.80
	Pt	.25	3.7	3.0	2.4
	W	.20	4.2	3.4	2.7

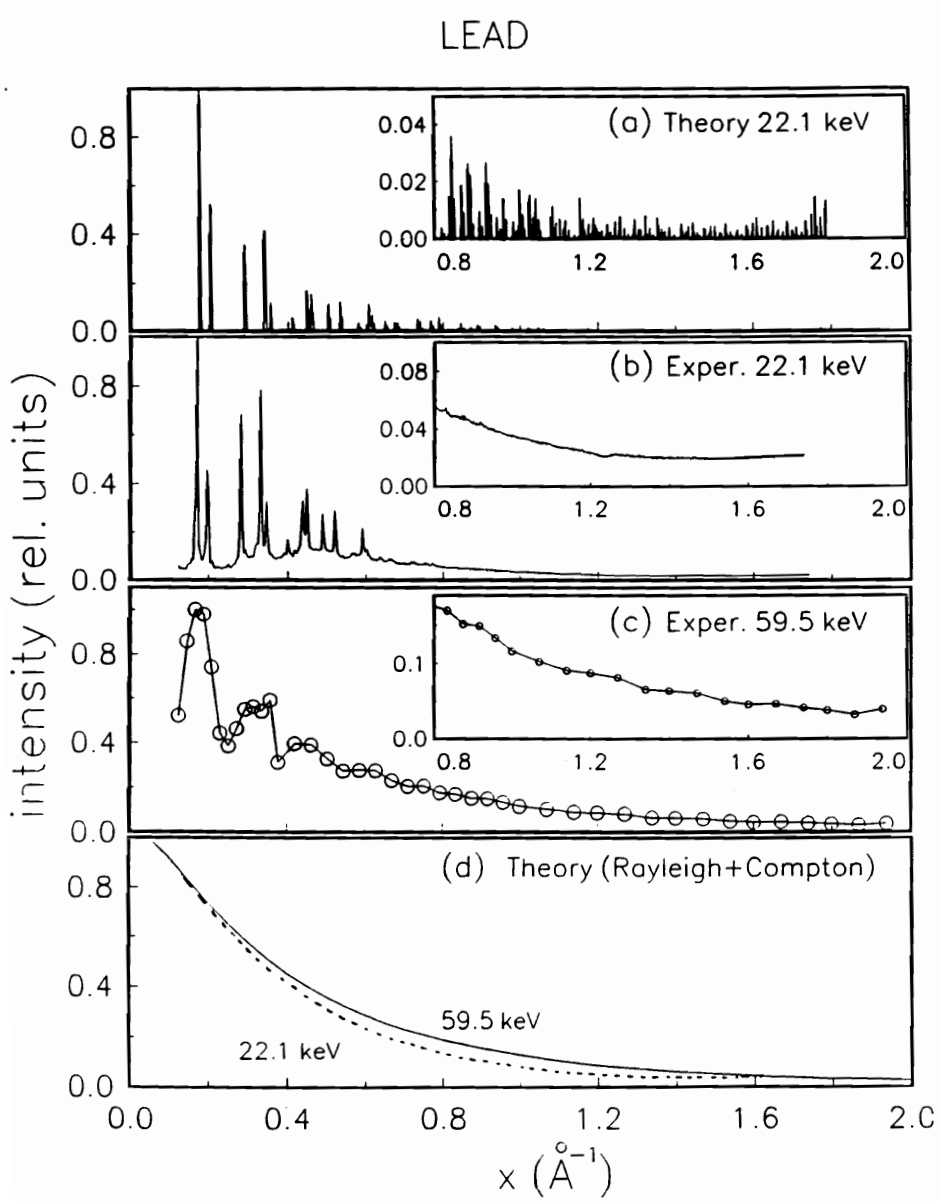
LEAD
(a) Theory 22.1 keV
(b) Exper. 22.1 keV
(c) Exper. 59.5 keV
(d) Theory (Rayleigh+Compton)
59.5 keV
22.1 keV
intensity (rel. units)
x (Å^{-1})

fig 1

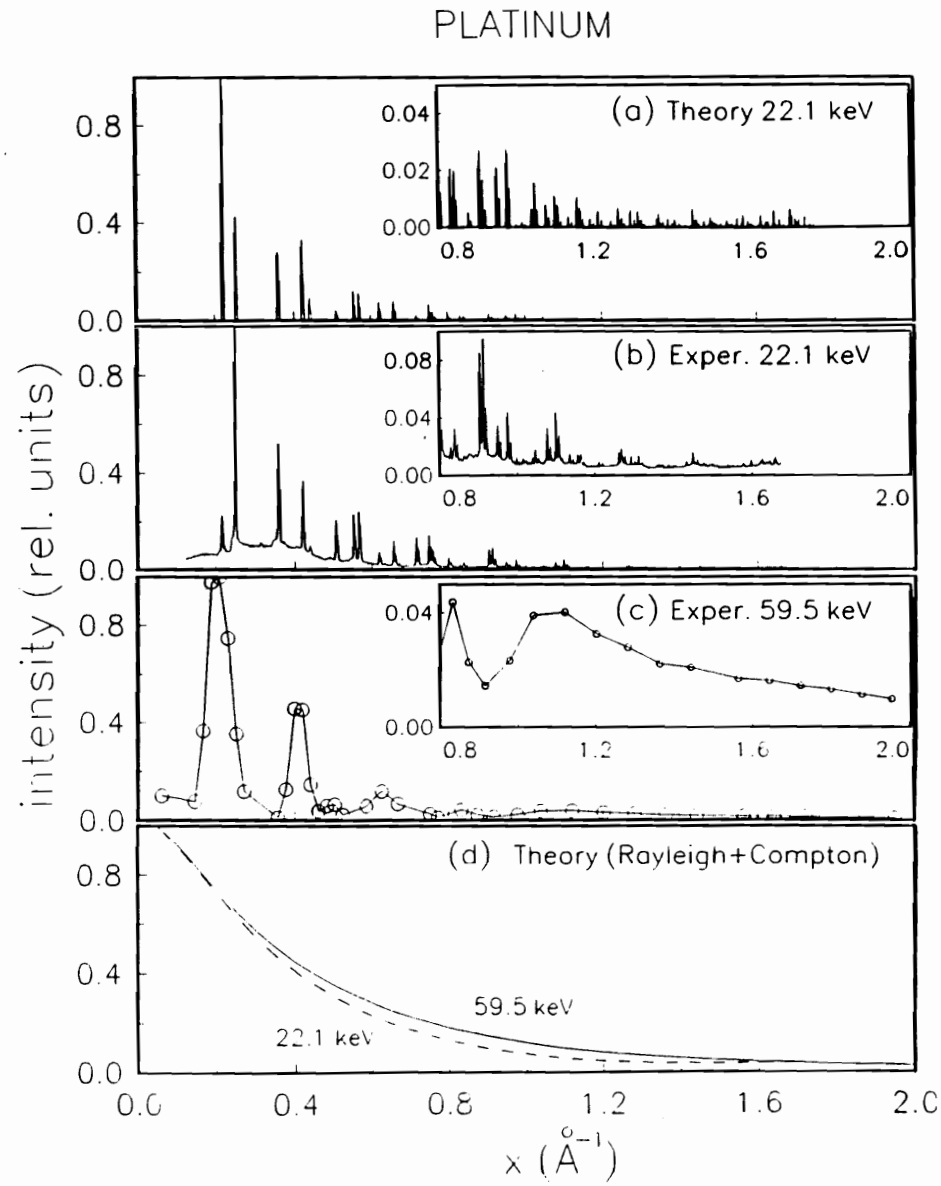
PLATINUM
(a) Theory 22.1 keV
(b) Exper. 22.1 keV
(c) Exper. 59.5 keV
(d) Theory (Rayleigh+Compton)
59.5 keV
22.1 keV
intensity (rel. units)
x (Å^{-1})

fig 2

WOLFRAM

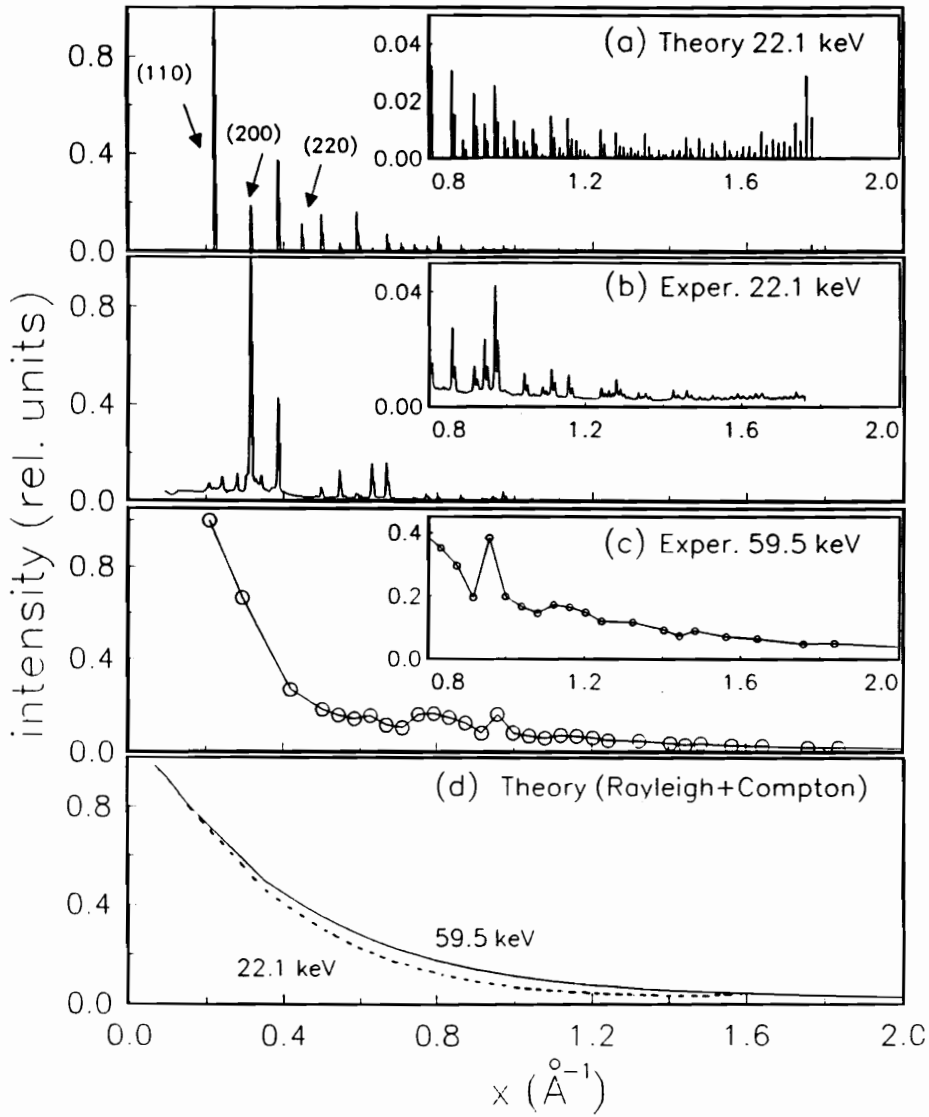

fig 3