ANGULAR DEPENDENCE OF THE X-RAY RAMAN SCATTERING INTENSITY FROM POLYCRYSTALS

A.N.Andriotis

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,48 Vassileos Constantinou Ave., Athens 501/1, Greece

and
C.A.Londos

Physics Department,University of Athens, 104 Solonos Str., Athens 144, Greece

It is shown that the existing discrepancy in the anglular dependence of the X-ray Raman scattering intensity from polycrystals, which results from calculations in the dipole approximation and from calculations which take the electromagnetic interaction completely into account, is due to the way the polycrystalline limit is considered. An application to Be-polycrystals is also presented.

The inelastic scattering of X-rays with light elements (Li,Be,C,B) and their compounds results among others and in observable spectra which are related to excitations of the valence electron or/and to excitations of localized inner-shell electrons. Large momentum transfers during the scattering result in the excitation of the valence and core electrons with high kinetic energy and this type of scattering is the well known Compton scattering[1-2]. For small momentum transfers the scattering process favors the excitation of inner shell (localized) electrons into states with energies near the Fermi energy. The later type of scattering is known as X-ray Raman scattering[3-4]. The mathematical expression for an X-Ray Raman scattering to take place is:

$$ a\ P = \frac{4\pi a}{\lambda}\ \sin\frac{\vartheta}{2}\ \leqslant 1 \qquad (1) $$

where a is the radius of the orbit of the core electron, P is the magnitude of the momentum transfer vector, ϑ is the scattering angle, and λ is the wave length of the incident radiation which in addition has to be of frequency $\dot{v}$ such as $h v \gg E_o$ where E_o is the binding energy of the core electron.

The quantum-mechanical theory of the X-Ray Raman scattering has been given in a work by Mizuno and Ohmura. Mizuno and Ohmura[3] (to be referred as MO) employed the dipole approximation and obtained the following angular dependence of the scattering intensity, R_{MO}, in the case of polycrystals:

$$ R_{MO} = \frac{R'_{MO}}{1+\cos^2\vartheta}\ \sim\ \sin^2\frac{\vartheta}{2} \qquad (2) $$

A few years later, Babuskin[5-6] generalizing the work of MO introduced hydrogenic type of wave functions in order to describe the K-shell electrons and worked out the general case without restricting to the dipole approximation. Babuskin's result for the scattering intensity, R_B, from polycrystals has the following dependence on the scattering angle:

$$ R_B = \frac{R'_B}{1+\cos^2\vartheta}\ \sim\ \frac{1}{(1+\sin^2\frac{\vartheta}{2})^4} \qquad (3) $$

Thus Babuskin concluded that the angular dependence of the scattering intensity upon the scattering angle has a Compton like profile with finite amplitude at $\vartheta=0$, in contrary to MO result.

On the other hand the experimentally obtained intensity profiles exhibit a behaviour which supports the results of MO for small scattering angles. However for bigger scattering angles the experimental results decline appreciably from the predictions of MO theory[7-11].

It was then suggested that agreement between theory and experiment may be achieved if terms higher than the dipole approximation term could be included in the theory of MO.

These discrepancies between the existing theories and the lack of a satisfactory description of the experimental data, have incite us to review this problem in the present work. In the next paragraphs we describe the basic reason for the existing differences between the two theoretical approximations to the X-ray Raman spectra, i.e., the difference between the theory which takes into account the electromagnetic interaction completely and the theory which considers the electromagnetic interaction in the dipole approximation. Finally we will present the results from an application on Be polycrystals.

The right hand side of eqn.(2) and (3) results from the dependence of the modulus square of the transition probability amplitude, $\langle f|V'|i\rangle$, upon the scattering angle. By $|f\rangle$ and $|i\rangle$ we denote, respectively, the final and the initial states of the electrons which undergo the transition due to a perturbation V' induced by the electromagnetic field. Keeping only the trerm of this perturbation which depends on the square of the electromagnetic vector potential A , it can be shown that, within a constant, the scattering intensity R' is:

$$R' = (1+\cos^2\vartheta)\left|\left\langle f\left|e^{i\vec{P}\cdot\vec{r}}\right|i\right\rangle\right|^2 \qquad (4)$$

from which we define the following angular scattering profile:

$$R = \frac{R'}{1+\cos^2\vartheta} = \left|\left\langle f\left|e^{i\vec{P}\cdot\vec{r}}\right|i\right\rangle\right|^2 \qquad (5)$$

$\vec{P}$ is the momentum transfer vector, i.e.,

$$\vec{P} = \vec{p}-\vec{p}_o \qquad (6)$$

where $\vec{p}$, $\vec{p}_o$ are the wave vectors of the incident and scattered radiation respectively. Since $|\vec{p}| \cong |p_o|$, the absolute value of the transfer momentum vector takes the form

$$P = 2p_o\sin\frac{\vartheta}{2} = 2\frac{\omega_o}{c}\sin\frac{\vartheta}{2} \qquad (7)$$

where ω_o is the frequency of the incident radiation and c is the velocity of light.

The dipole approximation to eqn.(5) consists of replacing $\langle f|\exp(i\ \vec{P}\cdot\vec{r})|i\rangle$ by its first non-vanishing term which is $\langle f|i\vec{P}\cdot\vec{r}|i\rangle$ under the condition $\langle f|i\rangle = 0$.

Babuskin[6] worked with the complete expression given by eqn.(5). He employed an OPW function for the final state of the scattered electron and he used a hydrogenic function in order to describe the local K-shell electron which undergoes the scattering. His result (eqn. (12) of reference 6) is applicable in the cases of perfect crystalline samples and it should be pointed out that this result predicts a zero transition probability amplitude for any final electron state if the momentum transfer vector is zero. In other words Babuskin's result predicts zero Raman scattering intensity at zero scattering angle for any final electron state. However after averaging over all possible final states Babuskin obtained[6] an intensity profile which exhibits finite scattering intensity at zero scattering angle and which holds true in the polycrystalline limit.

On the other hand, Mizuno and Ohmura[3] in order to derive an expression for the scattering intensity in the polycrystalline limit (and in the dipole approximation) argued that this limit may be obtained by averaging a ϑ-independent matrix element T, namely the matrix element

$$T(\omega)= \sum_{\substack{f \\ unoccupied}} \langle i|\vec{r}|f\rangle\langle f|\vec{r}|i\rangle\ \delta(\omega-\epsilon_f-\epsilon_i) \qquad (8)$$

where $\vec{r}$ is the dipole operator, ϵ_f and ϵ_i are the eigenenergies of the final and initial state respectively.

It should be noted, however, that in the case where we are not restricted to the dipole approximation the averaging over all possible final states is mostly associated with the averaging of the direction between the momentum transfer vector $\vec{P}$ and the electron momentum vector $\vec{k}$ (of the final state), a situation which is avoided in the dipole approximation of MO. Thus on the one hand the procedure of MO[3] or equivalently the dipole approximation is equivalent of averaging firstly the direction between $\vec{P}$ and $\vec{k}$ and then

calculate the transition probability amplitude. On the other hand in Babuskin's procedure, or equivalently in the case where the electromagnetic interaction is taken completely into account, the transition probability amplitude is calculated firstly and then this is averaged over all possible final states.

The two averaging procedures are not equivalent and this becomes clear if both averaging schemes are applied in Babuskin's result(eqn(12) of reference 6).

In the present work we employed the Hartree-Fock atomic states to describe the initial states of the core electrons. Linear combinations of Gaussian functions were used with coefficients obtained from the solution of the Hartree Fock Hamiltonian of the free atom[12]. Thus our initial state $|i\rangle$ is:

$$|i\rangle = \psi_{nlm}(\vec{r}) = (\sum_p c_{np} \, g_{np}(r)) \, Y_{lm}(\vartheta, \varphi) \qquad (9)$$

where c_{np} are numerical coefficients and $g_{np}(r)$ are gaussian functions. The final state is assumed to be a free electron state which is taken orthogonal to all core states of the scatterer. The core states $\psi_a(\vec{r})$ of the scatterer are given with expressions similar to eqn(9) and were obtained from the solution of the free atom[12]. Thus our final state $|f\rangle$ is

$$|f\rangle = \frac{1}{\sqrt{\Omega}} \, e^{i\,\vec{k}.\vec{r}} - \sum_\alpha \gamma_\alpha \psi_\alpha(\vec{r}) \qquad (10)$$

where Ω is the volume of the system, α is a set of quantum numbers which describe the core states and the coefficients γ_α are obtained from the requirement $\langle f | \psi_\alpha \rangle = 0$.

The analytic form of the initial and final states employed in this work, allows to calculate the transition probability amplitude $\langle f | V' | i \rangle$ mostly analytically with a result of limited numerical errors. Also the use of exact Hartree-Fock initial states will result not only in estimations which allow better comparison with experiment but also in conclusions about the effect of the initial states on the X-ray Raman spectra.

Finally, in order to describe the polycrystalline limit, we firstly find the transition

probability amplitude and then we average this over all possible final states. This averaging procedure, averages over all possible directions of the wave vector $\vec{k}$ of scattered electron while its magnitude is assumed constant and equal to the Fermi wavevector k_F. For comparison the other averaging scheme was also employed. In other words the angle between the vectors $\vec{P}$ and $\vec{k}$ was averaged firstly, and then the probability amplitude was calculated.

According to the previous paragraph we calculated the square , R, of the transition probability amplitude for X-ray Raman transitions in Be polycrystals. X-rays of frequency $\omega=218.6$ au were used and the obtained Raman spectra R=f(ϑ), in the two averaging schemes are presented in Fig.1. As it is seen from Fig.1 the two averaging schemes exhibit similar trends: Both profiles become zero for zero momentum transfer or zero scattering angle. However both profiles decline appreciably from the linear profile of the dipole approximation. It is only in the region of scattering angles between $45°-90°$ where our profiles exhibit a linear behaviour. This linear
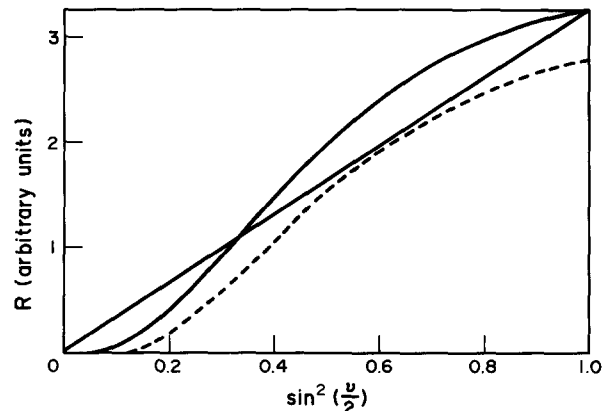

Fig.1 Angular dependence of the X-ray Raman scattering intensity from polycrystals in a calculation which takes the electromagnetic interaction completely into account. The full curve corresponds to the case where the polycrystalline limit is taken by averaging the transition probability amplitude over all final electron states. The straight line is the corresponding result expected by treating the electromagnetic interaction in the dipole approximation. The dashed curve corresponds to the case where the direction of the wave vector of the final state of the electrons is averaged firstly and then the transition probability amplitude is calculated.

part however does not pass through the origin as it would have been expected according to recent experimental information[10]. But it should be emphasized that data of X-Ray Raman spectra for scattering angles $<30^{\circ}$ are very rare (to our knowledge) and therefore the validity of the dipole approximation could be questioned for small scattering angles.

It is clear from Fig.1 that the effect of the complete incorporation of the electromagnetic interaction in deriving the transition probability of the X-Ray Raman scattering as compared to the results in the dipole approximation, is that the Raman scattering intensity appears lower for small scattering angles and enhanced for higher angles.

Thus the present results are closer to the findings of MO as well as to the experimental data. On the other hand Babuskin's results may be applicable in cases where the scatterer is a perfect crystal whereas in cases of polycrystalline scatterers it has been shown that his results are dependent on the way the polycrustalline limit is incorporated. In concluding it should be emphasized how important is the averaging procedure over final states or in other words the way the polycrystalline limit is achieved. As our initial states do not exhibit any significant sensitivity with respect to the averaging schemes employed, they appear more efficient than the hydrogenic type of solutions employed so far.

REFERENCES

1. P.Eisenberger and P.M.Platzman,Phys.Rev.A2, 415(1970).

2. M.Cooper,Advances in Physics 20,453(1971)

3. Y.Mizuno and Y.Ohmura,J.Phys.Soc.Japan,22, 445(1967)

4. M.Kuriyama,Acta Cryst.,A27,634(1971)

5. F.Babushkin,Izv.Vuzor,Ser.Fizika No9,26 (1971).

6. F.Babushkin,Acta Physica Polonica,A40,183 (1971)

7. T.Suzuki,J.Phys.Soc.Japan,22,1139(1967).

8. T.Suzuki,T.Kishimoto,T.Kaji and T.Suzuki, J.Phys.Soc.Japan 29,730(1970)

9. T.Suzuki and H.Nagasawa,J.Phys.Soc.Japan, 39,1579(1975)

10. D.Papademitriou and D.Miliotis,J.Phys.Soc. Japan 51,2966(1982)

11. C.Koumelis and C.A.Londos,Canadian J.Phys. 58,1507(1980)

12. C.C.J.Roothaan   and P.Bagus,Methods in Computational Physics,Vol.2, Academic Press,New York(1963)