Pramāṇa, Vol. 1, No. 3, 1973, pp. 147-54. Printed in India.

Plasmon excitation in the x ray absorption process

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MS received 3 May 1973; in final form 28 June 1973

Abstract. A simple approach is developed to study the excitation of a plasmon due to valence electronic correlations in the x ray absorption process. Assuming a complete separation between the core and the valence electrons, we introduce the plasmons in the system Hamiltonian externally according to the Bohm-Pines collective formalism and carry out the corresponding canonical transformations to separate the x ray photon-plasmon-electron term. According to our calculations, the relative intensity of the plasmon process with respect to the main absorption, which represents single particle excitations is 0·12 times the interelectronic separation measured in Bohr radii. The theoretical estimates of the plasmon intensity agree satisfactorily with the experimental values for the Mn K and the Re L_{III} absorption discontinuities.

The shape of the plasmon absorption band resembles the main absorption edge, if the wave vector dependence of the plasmon frequency is neglected. The intensity of the second plasmon harmonic is about 3 per cent of the first plasmon satellite spectrum. The electron plasmon interaction modifies the shape of the plasmon spectrum.

Keywords. Plasmon; x ray absorption; x ray spectroscopy.

1. Introduction

The valence electrons in a solid can be considered to constitute a quantum plasma. Many workers have investigated the effects of the plasmons, quanta of plasma oscillations, on the various physical properties of solids (Pines 1955, Hedin and Lundquist 1969). Pimpale and Mande (1973) have shown that the plasmon excitation produces a modification in the quasi electron spectrum.

In recent years considerable experimental and theoretical work has been reported on the plasmon excitation in x ray inelastic scattering (Suzuki and Tanokura 1970, Priftis 1970, Alexandropoulos 1971, Ohmura and Matsudiara 1964, Pimpale and Mande 1971) and x ray emission processes (Rooke 1963, Brouers 1967, Hedin 1968, Glick *et al* 1968) in light metals. The possibility of such a plasmon excitation in the x ray absorption process giving rise to a characteristic peak in the absorption spectra was suggested by Ferrell (1956) and Nozières and Pines (1959). However, the plasmon effects in x ray absorption have not been studied extensively. In this paper we present a simple approach to calculate the intensity and shape of the plasmon peak in x ray absorption spectra using the Bohm-Pines (1953) canonical transformation technique.

2. Physical concepts

Let us consider the processes of x ray emission and absorption in solids in a simplified manner. In x ray emission, the valence electrons jump to an inner level (as shown in figure 1 a) in which a hole has earlier been created either by direct electron bombard-

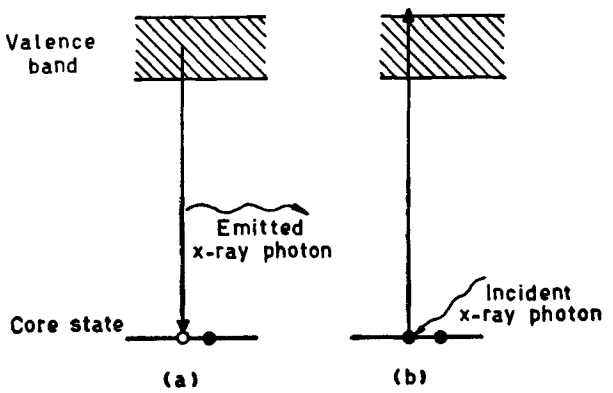

Figure 1. First order x ray transitions in a solid, a: emission; b: absorption.

ment or by fluorescence excitation. Hence, in the x ray emission process one must consider the presence of a core state vacancy in the initial state and, therefore, the interaction between the valence electrons and the bound positive hole has to be taken into consideration. In the x ray absorption process, as shown in figure 1 b, the ejected electron goes to an available empty state in the valence band leaving behind a hole in the core state. Hence, a first order x ray transition couples a valence electron state with the core state. It is well known that the many body character of the valence electrons may be taken into consideration by invoking the plasmon concept. Although a direct x ray photon-plasmon interaction is not possible, since one represents a transverse mode and the other a longitudinal mode, the disturbance of the valence electrons in an x ray transition may give rise to plasmon excitation (Parratt 1959).

To start with, we assume that the core electrons and the valence electrons are completely separated from each other, so that the Coulomb interaction between them has been taken into consideration in obtaining their respective wave functions. We may then consider the valence electrons to be plane waves (free particles) interacting with one another through Coulomb interaction, and we need no more consider the interaction between the valence and the core electrons.

In x ray emission, due to the presence of the core hole in the initial state, the plasmon eigenfields of the negative valence electrons and the positive hole interfere destructively (Brouers 1967), thus reducing considerably the intensity of the plasmon peak in the emission band. In x ray absorption, however, this destructive interference is absent, and hence one may expect a relatively more intense plasmon peak.

Roulet *et al* (1969) and Nozières and de Dominicis (1969) have shown that in first order x ray transitions the initial and the final states of the system do not conform to the same Hamiltonian. The interactions arising out of this situation may sometimes give rise to a many body singularity in the vicinity of the Fermi limit due to the possibility of the excitation of a large number of electrons very close to the Fermi surface. In the calculations described below the explicit effects of these final state interactions on the plasmon band have not been taken into consideration. However, we automatically take into account these effects, since we correlate the plasmon spectrum with the main absorption spectrum in the calculation of which these final state interactions can be taken into consideration.

3. Formulation of the problem

The model Hamiltonian $\mathcal{H}$ describing the system comprising the core and the valence

electrons can be written as

$$\mathcal{H}=\mathcal{H}_{\text{core}}+\mathcal{H}_{\text{val}}$$
$$=\sum_i \epsilon_i a_i^\dagger a_i+\sum_p \frac{\hbar^2 p^2}{2m} c_p^\dagger c_p+\tfrac{1}{2}\sum_{\substack{k\neq 0,\\ p,\,q}} M_k^2\,[c_{p+k}^\dagger c_{q-k}^\dagger c_q c_p-\mathcal{N}] \tag{1}$$

where $a_i^\dagger$ and a_i are the creation and the annihilation operators for the electrons in the core state $|i\rangle$ and ϵ_i is the corresponding energy, $c_p^\dagger$ and c_p are the creation and the annihilation operators for the valence electrons (the spin index is suppressed for simplicity), $M_k^2=4\pi e^2/k^2$ is the Fourier transform of the Coulomb interaction and $\mathcal{N}$ is the number of valence electrons per unit volume.

In order to obtain the plasmons, following Bohm and Pines (1953), we introduce extra collective coordinates in equation (1). The model Hamiltonian then becomes

$$\mathcal{H}=\mathcal{H}_{\text{core}}+\mathcal{H}_{\text{val}}+\mathcal{H}_{\text{coll}} \tag{2}$$

where

$$\mathcal{H}_{\text{coll}}=\sum_{k<k_c}\frac{P_k^\dagger P_k}{2}-\mathrm{i}\sum_{k<k_c,\,p} M_k P_k c_{p-k}^\dagger c_p \tag{3}$$

These additional terms, in which P_k is the momentum variable for the plasmon field and k_c is the magnitude of the plasmon cut off wave vector, represent respectively the kinetic energy of the plasmon field and its interaction with the valence electrons.

Due to the introduction of the new field variables the degrees of freedom of the system are increased by $k_c^3/6\pi^2$. In order to take them into account a set of $k_c^3/6\pi^2$ subsidiary conditions are imposed so that the eigenfunctions of the Hamiltonian (Eq 2) which satisfy the subsidiary conditions are also the eigenfunctions of eq 1. The subsidiary conditions for k varying between zero to k_c are

$$P_k\,|\,\Psi\,\rangle=0 \tag{4}$$

where $|\,\Psi\,\rangle$ is the eigenfunction of equation (2).

Now, in order to describe the interaction between x rays and the electrons, we represent the incident photon field by a vector potential, expand it in a Fourier series in a unit volume and introduce the photon creation and annihilation operators. The process of x ray absorption is then described by adding the following term $\mathcal{H}_{\text{abs}}$ to the Hamiltonian (Eq 2).

$$\mathcal{H}_{\text{abs}}=\sum_{l>p_0} V(\boldsymbol{l})\,c_{\boldsymbol{l}}^\dagger\,a_i\alpha+\text{c.c.} \tag{5}$$

where c.c. denotes the complex conjugate, α is the photon destruction operator and p_0 is the value of the wave vector at the Fermi surface. $V(\boldsymbol{l})$ is proportional to the corresponding matrix element for the x ray absorption process involving the transition of an inner level electron (in core state ϕ_i) to the valence level of momentum $\hbar\boldsymbol{l}$ (wave function $\phi_{\boldsymbol{l}}$). One may then write

$$V(\boldsymbol{l})\propto\langle\,\boldsymbol{l}\,|\,M\,|\,i\,\rangle=\int\phi_{\boldsymbol{l}}^*\,\boldsymbol{e}\,\exp(\mathrm{i}\boldsymbol{k}.\boldsymbol{r}).\boldsymbol{p}\phi_i\mathrm{d}\tau \tag{6}$$

where $\boldsymbol{e}$ and $\boldsymbol{k}$ are respectively the polarization and wave vectors of the absorbed photon.

Thus, our final Hamiltonian which includes the absorption process consists of the following terms:

$$\mathcal{H}=\mathcal{H}_{\text{core}}+\mathcal{H}_{\text{val}}+\mathcal{H}_{\text{coll}}+\mathcal{H}_{\text{abs}} \tag{7}$$

Since the subsidiary conditions do not depend in their final form upon the plasmon variables (Bohm and Pines 1953), and are relatively small in number, we shall neglect them in calculating the plasmon spectrum.

We carry out a canonical transformation generated by the operator S given by

$$S=-\mathrm{i}\sum_{k<k_c,\ p} M_k Q_k c^\dagger_{p+k} c_p \tag{8}$$

where Q_k is the field coordinate conjugate to the momentum variable P_k and satisfies the commutation relation

$$[P_k, Q_{k'}]=-\mathrm{i}\hbar\delta_{kk'} \tag{9}$$

The canonical transformation leaves the core term in equation (7) unmodified and separates $\mathcal{H}_{\mathrm{val}}$ and $\mathcal{H}_{\mathrm{coll}}$ into terms representing the plasmons, individual valence electrons with modified electron-electron interaction, and linear and nonlinear interactions between the plasmons and the valence electrons. As an effect of the transformation the $\mathcal{H}_{\mathrm{abs}}$ term yields an additional new term $\mathcal{H}_{\mathrm{add}}$ and several higher order terms. It can be shown from equations (5) to (8) that

$$\mathcal{H}_{\mathrm{add}}=\frac{1}{\hbar}\sum_{\substack{k<k_c,\\ p>p_0}} V(\boldsymbol{p}-\boldsymbol{k}) M_k Q_k c^\dagger_p a_i \alpha \tag{10}$$

It is convenient to introduce in equation (10) the plasmon creation and annihilation operators $A^\dagger_k$ and A_k defined by

$$Q_k=(\hbar/2\omega_{\mathrm{p}})^{1/2}\cdot(A_k+A^\dagger_{-k}) \tag{11}$$

where ω_{p} is the plasma frequency and is equal to $(4\pi\mathcal{N}e^2/m)^{\frac{1}{2}}$.

Equation (10) could then be rewritten as

$$\begin{aligned}\mathcal{H}_{\mathrm{add}}=(1/2\hbar\omega_{\mathrm{p}})^{1/2}\cdot\sum_{\substack{k<k_c,\\ p>p_0}} M_k V(\boldsymbol{p}-\boldsymbol{k}) A_k c^\dagger_p a_i \alpha + \\ +(1/2\hbar\omega_{\mathrm{p}})^{1/2}\cdot\sum_{\substack{k<k_c,\\ p>p_0}} M_k V(\boldsymbol{p}+\boldsymbol{k}) A^\dagger_k c^\dagger_p a_i \alpha\end{aligned} \tag{12}$$

The first and the second terms of equation (12) describe respectively the absorption and emission of a plasmon of momentum $\hbar\boldsymbol{k}$ accompanying x ray absorption.

The higher order terms in equation (10) represent the processes in which more than one plasmon participate and are discussed in Appendix 1. It will be seen that the intensities of these processes are very much weaker than the one plasmon process. We, therefore, neglect in our calculations the higher order plasmon processes.

4. Calculations

Neglecting the polarization of the plasmons due to the electron-plasmon interaction, the matrix element for the process, in which the absorption of an x ray photon is accompanied with the simultaneous emission of a plasmon of momentum $\hbar\boldsymbol{k}$ when a core electron from state $|\mathrm{i}\rangle$ is removed and an electron in the momentum state $\hbar\boldsymbol{p}$ is added to the valence band, is found to be

$$(1/2\hbar\omega_{\mathrm{p}})^{1/2}\cdot V(\boldsymbol{p}+\boldsymbol{k})\cdot M_k \qquad \text{with } p>p_0 \tag{13}$$

Using Fermi's golden rule, the cross section for the process is obtained as (Schiff 1955)

$$\sigma[\hbar\omega_p(\boldsymbol{k})] = \frac{1}{c} \cdot \frac{2\pi}{\hbar} \cdot |V(\boldsymbol{p}+\boldsymbol{k})|^2 \cdot M_{\boldsymbol{k}}^2 \cdot \frac{dN}{dE} \tag{14}$$

where dN/dE is the energy density of states for electron at $\hbar^2p^2/2m$ and plasmon at $\hbar\omega_p(\boldsymbol{k})$.

If we assume as is customary, that the matrix element for the main x ray transition involving a single electron jump varies slowly with p, we can approximate equation (14) to

$$\sigma[\hbar\omega_p(\boldsymbol{k})] = \sigma_{abs} M_{\boldsymbol{k}}^2 / 2\hbar\omega_p(\boldsymbol{k}) \tag{15}$$

where σ_{abs} is the cross section for the main absorption.

The plasmon energy under the present approximation does not depend on the wave vector $\boldsymbol{k}$. The intensity of the plasmon peak relative to the main absorption intensity, therefore, is given by

$$\sigma(\hbar\omega_p)/\sigma_{abs} = \sum_{k<k_c} M_{\boldsymbol{k}}^2 / 2\hbar\omega_p = e^2 k_c / \pi\hbar\omega_p \simeq 0{\cdot}12\, r_s \tag{16}$$

where r_s is the radius of the unit sphere in Bohr units.

Equation (16) represents the ratio of the long range part of the Coulomb interaction energy to the plasmon energy. This expression enables a direct comparison of the two absorption processes with experimental results, which is discussed in the next section. It is also clear from equation (16) that the shape of the plasmon absorption band would be similar to the main absorption edge.

The effect of the electron-plasmon interactions on the plasmon absorption band, as a consequence of which the plasmon frequency becomes wave vector dependent, is discussed in Appendix 2.

5. Comparison with experimental results

As compared to the available experimental work on the plasmon satellites in x ray emission spectra, very little experimental work is reported on the plasmon peak in x ray absorption spectra. A survey of the existing experimental data (Joshi 1967, Mande and Joshi 1968, 1969, Bhide and Bhat 1969, Bahl 1971, Pendharkar and Mande 1973) reveals that in the extended fine structure on the high energy side near the main x ray absorption discontinuities, the first or the second structure corresponds to the plasmon spectrum. In order to estimate the intensity of the plasmon peak it is necessary to separate it from the main absorption spectrum. The unfolding of the spectrum is, in general, very difficult since the experimental curves are not corrected for the instrumental factors; besides they do not represent the true variation in the absorption coefficient. The separation of the plasmon peak is further complicated due to the overlap problems. However, in the case of the Mn K and the Re L_{III} absorption discontinuities, as reported by Joshi (1967) and Pendharkar and Mande (1973) respectively, the separation of the plasmon peak is facilitated due to the existence of a prominent white line close to the main edge. We have, therefore, compared our calculated intensities with the experimental values in these two cases only.

These spectra are reproduced here in figures 2 and 3. We have resolved in these two figures the whole spectrum into the main absorption edge and the superposed absorption lines representing the fine structure, following the method suggested by Hayasi (1951). The intensity of the plasmon peak is then measured relative to the main absorption jump.

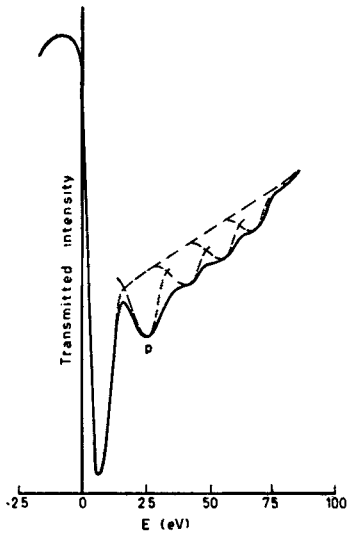

Figure 2. Resolution of the Mn K absorption discontinuity in terms of the main edge and the superposed fine structure lines. p refers to the plasmon peak.

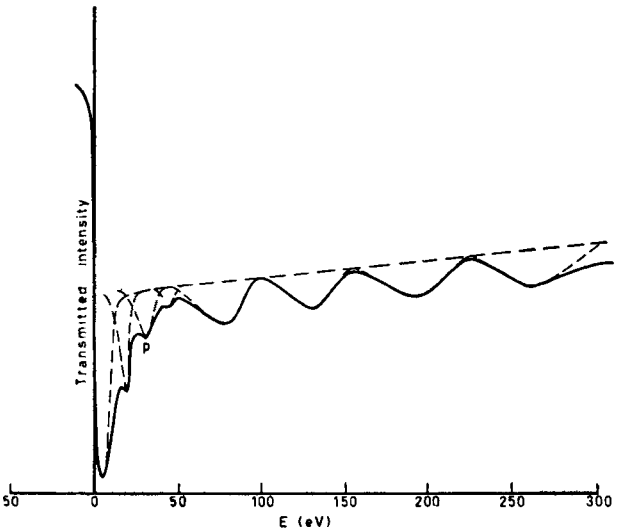

Figure 3. Resolution of the Re L_{III} absorption discontinuity in terms of the main edge and the superposed fine structure lines. p refers to the plasmon peak.

Table 1. Theoretical and experimental estimates of the intensity of the plasmon peak relative to the main absorption intensity for the Mn K and the Re L_{III} discontinuities.

Element	$\hbar\omega_p$ (eV)	k_c (Å^{-1})	$\sigma(\hbar\omega_p)/\sigma_{abs}$	
			Calculated	Experimental
Mn	28	1·08	0·17	0·15
Re	26	1·04	0·18	0·13

The theoretical value of the intensity of the plasmon peak relative to the main absorption jump is calculated from equation (16). This calculation requires the values of $\hbar\omega_p$ and k_c. Though experimental values of the plasmon energy are available, the corresponding values of k_c are not available in the literature. In order to bring harmony, we have used the theoretical values of the plasmon energy and the cut off wave vector k_c as calculated from the following formulae (Pines 1955).

$$\hbar\omega_p=\hbar(4\pi Ne^2/m)^{1/2};\ k_c=0{\cdot}353\ r_s^{1/2}\ p_0 \tag{17}$$

The values of $\hbar\omega_p$, k_c and the theoretical and experimental estimates of the relative intensities of the plasmon peak with the main absorption jump for the Mn K and the Re L_{III} discontinuities are tabulated in table 1. The agreement between the theoretical and experimental results is quite satisfactory.

6. Concluding remarks

Very recently, during the writing of this paper, we came across an interesting paper by Ting (1972) on this very subject. He has theoretically analysed the plasmon processes in x ray absorption and emission using the parquet diagram technique. However, he

has not been able to calculate explicitly the shape and intensity of the plasmon peak in x ray absorption spectra. Our results [equations (16) and (A 5)] are more specific and are directly applicable to the experimental situation.

Although several approximations are involved in our theoretical calculations, their main merit lies in inherent simplicity. Even if more elaborate theoretical calculations are made, it would not be possible to compare them with the experimental results because of the approximate character of the experimental curves.

Appendix 1: Higher order plasmon terms

A typical second order term which involves creation of two plasmons is given by

$$\mathcal{H}_{\text{add}}\ (2\ \text{plasmons}) = \frac{1}{4\hbar\omega_{\text{p}}} \cdot \sum_{\substack{k,k'<k_{\text{c}},\\ p>p_0}} \left[V(\boldsymbol{p}+\boldsymbol{k}+\boldsymbol{k}')M_{\boldsymbol{k}}M_{\boldsymbol{k}'} \cdot A_{\boldsymbol{k}}^{\dagger}A_{\boldsymbol{k}'}^{\dagger}c_{\boldsymbol{p}}^{\dagger}a_{\mathrm{i}\boldsymbol{\alpha}} \right] \tag{A 1}$$

Similar equations can be written for the processes involving absorption of two plasmons, and creation and absorption of one plasmon each.

From equations (A 1) and (13) it is seen that the intensity of the two plasmon process as compared to the one plasmon process is given by

$$\frac{\text{Intensity (2 plasmons)}}{\text{Intensity (1 plasmon)}} = \sum_{k<k_{\text{c}}} \frac{M_{\boldsymbol{k}}^2}{8\hbar\omega_{\text{p}}} \simeq 0{\cdot}03 \tag{A 2}$$

The intensities of further higher order processes are even smaller, thus making it unnecessary to consider the plasmon processes involving more than one plasmon.

Appendix 2: Electron-plasmon interaction effects

The electron-plasmon interaction is almost completely eliminated (within random phase approximation) by the Bohm-Pines (1953) second canonical transformation. When this transformation is carried out, a new term representing the creation of a plasmon in x ray absorption in addition to $\mathcal{H}_{\text{add}}$ [equation (10)] appears. The plasmon frequency becomes wave vector dependent, and for small values of k it is given by

$$\omega_{\text{p}}(\boldsymbol{k}) \simeq \omega_{\text{p}} + (3v_0^2/10\omega_{\text{p}})k^2 \tag{A 3}$$

where v_0 is the magnitude of the electron velocity at the Fermi surface.

The relative magnitude of this new term as compared with $\mathcal{H}_{\text{add}}$ [equation (10)] is given by

$$\frac{\hbar\boldsymbol{k}\cdot\hbar\boldsymbol{p}/m + \hbar^2k^2/2m}{\hbar\omega_{\text{p}}(\boldsymbol{k}) + \hbar\boldsymbol{k}\cdot\hbar\boldsymbol{p}/m - \hbar^2k^2/2m} \simeq 0{\cdot}1 \tag{A 4}$$

Thus, because of its low magnitude we may neglect the new term arising out of electron-plasmon interaction.

The shape of the plasmon absorption band is then easily obtained from equations (14) and (15) as

$$I_{\text{plasmon}}\ (E) = \sum_{k<k_{\text{c}}} \frac{I_{\text{abs}}\,[E-\hbar\omega_{\text{p}}(\boldsymbol{k})]\ M_{\boldsymbol{k}}^2}{2\hbar\omega_{\text{p}}(\boldsymbol{k})} \tag{A 5}$$

Since we do not expect the plasmon energy spread $[\hbar\omega_{\text{p}}(\boldsymbol{k}_{\text{c}})-\hbar\omega_{\text{p}}]$ to be more than a few electron volts, $E-\hbar\omega_{\text{p}}(\boldsymbol{k})$ varies only slightly from the Fermi energy. We can

then assume, as has been shown by Roulet *et al* (1969) and Nozières and de Dominicis (1969), the shape of the main absorption discontinuity to be given by

$$I_{\text{abs}}(E) = A/|\,\text{E}\,|^{\delta} \tag{A 6}$$

where A is a constant and δ is a critical exponent. For $\delta > 0$, there exists a singularity first suggested by Mahan (1967) in the main absorption spectrum.

From equations (A 3), (A 5) and (A 6) one obtains

$$I_{\text{plasmon}}(E) = \text{const.} \int_0^{k_c} \mathrm{d}k \left[\left(\hbar\omega_p + \frac{3\hbar v_0^2}{10\omega_p} k^2 \right) \cdot \left| \text{E} - \hbar\omega_p - \frac{3\hbar v_0^2}{10\omega_p} k^2 \right|^{\delta} \right]^{-1} \tag{A 7}$$

In general, this integral cannot be obtained in a closed form. However, for simple values of δ, it could be evaluated to yield the shape of the plasmon absorption spectrum. It may be noted that the singularity in the main absorption spectrum may get washed out in equation (A 7) due to the k dependence of the plasmon frequency.

Acknowledgements

One of us (AP) thanks the National Council of Educational Research and Training, New Delhi, for the award of the National Science Talent Search Scholarship.

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