Resonant satellites in photoemission and Auger spectra of d-band metals

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Photoemission and Auger electron spectroscopy are powerful tools in the study of the electronic and magnetic properties of d band metals. In certain instances experimental spectra can be directly interpreted as a measure of some one body density of states. In other cases one must consider the many body dynamics of the measurement process in detail. Striking examples of the latter are the resonant satellites in several filled d band materials which have been observed in photoemission near the photon energy threshold for core hole production. An elementary introduction to the physics of this satellite phenomenon will be presented. A model recently introduced by Davis and Feldkamp to explain resonant satellites in filled d band materials will be discussed in some detail and the predictions of this model will be used to illustrate some general properties of resonant photoemission satellites.

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Photoemission and Auger electron spectroscopy are powerful tools in the study of the electronic and magnetic properties of metals. In certain instances experimental spectra can be directly interpreted as a measure of some one-body density of states. In other cases one must consider the many body dynamics of the measurement process in some detail. Striking examples of the latter are the resonant photoemission satellites which have been observed near the photon energy threshold for core hole production. The purpose of this paper is to provide an elementary introduction to the subject, to examine the general model independent features of this phenomenon and to discuss one specific model mechanism of current interest.

Many core level spectroscopies which are receiving theoretical and experimental attention are concerned with the following general sequence of events. An electron is ejected from a core level in an atom or a solid by an incident particle (usually a photon or an electron) after which the core hole decays producing various final state products. This process is illustrated schematically in Fig. 1. It has been common practice in the past to treat various aspects of this process as separate, independent events, but the current emphasis is on treating this process as a unified, coherent whole.

For example in x-ray absorption spectroscopy one measures only the absorption rate for the initial photon and does not detect any of the final state decay products. The theorist models this process by "integrating out" the final state degrees of freedom. This results in an expression for the absorption rate which involves the density of states for the photoelectron convolved with a broadening function due to the finite lifetime of the core hole. While the fact that the hole does decay is considered, the particular states into which it decays are ignored. Thus x-ray absorption spectroscopy looks at the black box of Fig. 1 only from the "front end."

In contrast, x-ray emission spectroscopy is often viewed as a monitor of the decay of the core hole via photon production without reference to the existence of other possible decay products and often without reference to the mechanism by which the core hole was created. Likewise Auger spectroscopy monitors one or the other possible decay channels for the core hole.

It has recently become clear that one cannot simply base a theory of the decay channels on the initial existence of the core hole without reference to the process which created it. The unified theory of these processes maintains that they cannot be treated separately because of coherence between the initial production of the core hole and its final decay. This coherence is induced by the possibility of incomplete relaxation of the system in the intermediate state prior to the final decay event. This is a point of view which has not generally been taken in study of the satellite problem and is one which I would like to emphasize here.

A classic example which will be useful to understand before proceeding to photoemission satellites is the phenomenon of incomplete phonon relaxation in x-ray emission (1,2). A configuration coordinate diagram for this process is shown in Fig. 2. The essential physics represented here is that the phonons in a metal are displaced in the presence of the core hole potential. The simplest model of the emission process puts the system on path B in Fig. 2. One assumes that the system is in equilibrium in the presence of the core hole and that the phonons are then displaced when the electronic transition occurs. The resulting shake-up adds phonon satellites (in the form of Gaussian broadening) to the emission line shape.

This picture is too simple because the phonon system carries with it a memory of the process which created the core hole. The initial excitation of the core hole follows path A in Fig. 2. If the subsequent emission occurs quickly, the phonon coordinate will be near point a rather than b and there will be little energy transfer to the phonons (although the emission will still be phonon broadened (3,4)). If the emission occurs more slowly the phonon coordinate will be at some random point in its damped oscillatory trajectory between points a and c and one obtains a peculiar double humped emission spectrum arising from the fact that the system spends most of its time near the classical turning points (1). In either case the spectrum will be modified due to the incomplete relaxation of the phonon system in the intermediate state. The memory of the phonon system transfers a coherence between the input and output sides of the black box in Fig. 1. Despite the fact that the experiment is detecting only core holes which decay via photon emission, the duration of the intermediate state is determined not by the radiative width of the core hole but rather is limited by the Auger lifetime. Here is another clear example of why a unified picture is essential - in order to know what is happening in one channel one must know what is happening in all the others.

A closely analogous phenomenon is that of plasmon gain satellites (5). This comes about because the Auger decay takes place not in the equilibrium state of the plasmons but in an excited state produced by the initial creation of the core hole.

With an understanding of these coherence effects let us turn now to a discussion of the satellites observed in the photoemission/Auger spectra of d-band materials (6-9). Consider the simplified energy level diagram of Fig. 3a. Level A is a core level and B represents a shallow valence level, multiplet or other group of levels. The basic experiment of interest is constant initial state spectroscopy which monitors photoemission from B as a function of incident photon energy. It is found that there is an anomaly in the photocurrent as the photon energy is swept past the threshold for excitation of an electron out of A. The elementary particle theorist would refer to this as a natural consequence of the nitarity of the S-matrix. The sudden opening of a new channel propagates a disturbance through all the other channels. The mechanism through which this occurs is illustrated schematically in Fig. 3a. In addition to the direct photoemission from B, there is the possibility of an indirect process which begins with excitation of a core electron from level A into an unoccupied portion of B. This is followed by an Auger or autoionization process which refills A and ejects a fast electron. The energy of the fast electron may be equal to that of a directly photoemitted electron or slightly different thereby forming a satellite line near the direct photoemission line. There are numerous possibilities for different specific effects depending on the detailed nature and distribution of states in level B. It has been found that the general strength, location and shape of the satellite lines are useful for example in determining whether the valence excitations in various materials are band-like or atomic in character. These questions were surveyed at the last conference (10) and will therefore not be considered here.

Rather, I now turn to a more detailed analysis of a recent model for the photoemission satellite in filled d-shell materials such as Cu and Zn. This model put forth by Davis and Feldkamp (DF) (11) invokes an unusual mechanism which is interesting to investigate. Furthermore, the analytic solution of this model (12) exhibits several features common to resonant satellites in general and it therefore serves as a useful pedagogical example. The DF model considers the level scheme illustrated in Fig. 3b. A is a core level (such as Cu 3p), B is the valence d band (or other quasi-atomic level) and C is the sp conduction band.

It is convenient for the purposes of this analysis to follow DF and ignore direct photoemission from the d band and consider only the indirect process shown in Fig. 3b. This is probably a reasonable approximation since the satellite in Cu is seen readily only near resonance. Rather than thinking of the experiment as constant initial state spectroscopy of the d level, it is in this case better to view the experiment as monitoring the photoinduced ABB Auger spectrum as a function of photon energy. The usual picture of Auger spectroscopy would say that the photon energy is irrelevant as long as it exceeds the core excitation threshold. However a unified picture of the process shows the possibility of coherence between the initial core hole creation and the final Auger decay quite analogous to the example of x-ray emission described earlier. That is to say, the system remembers for a time how the core hole was created and in particular what photon energy was used. Referring to Fig. 3b one sees that this can occur because the final Auger decay takes place in the presence of a spectator electron which is a by-product of the creation of the core hole. For very high incoming photon energies this extra electron can be safely ignored since it leaves rapidly at high kinetic energy. However, for photon energies near threshold, the spectator electron can remain in the vicinity long enough to influence the final Auger process. The spectator electron is thus the vehicle via which coherence is transmitted from the excitation to the deexcitation process.

The DF model of this process is as follows. Prior to photoexcitation of the core electron, the conduction electrons obey a free particle Hamiltonian

$$H_0 = \sum_k \epsilon_k c_k^\dagger c_k \qquad (1)$$

After core level photoexcitation the conduction electrons as well as the photoexcited electron experience an attractive contact potential U at the site of the core hole. This introduces a scattering term H_1 into the Hamiltonian

$$H_1 = U \sum_{kk'} c_k^\dagger c_{k'} \qquad (2)$$

The subsequent Auger decay of the core hole leaves the system with two d holes which are assumed to be bound in a localized atomic state due to Coulomb correlations. These two holes produce a new scattering potential U' which is likely to be quite strong. Girvin and Penn (12) have obtained an approximate analytic solution to the DF model which is outlined below.

Let $R_Q(\omega)$ be the rate of production of Auger electrons in state Q with energy ϵ_Q as a function of photon energy ω. A generalized Fermi's golden rule gives

$$R_Q(\omega) = 2\pi \sum_k f_k \left| V_{kQ}(\omega) \right|^2 \delta(\omega - \epsilon_d - \epsilon_Q - \epsilon_k) \qquad (3)$$

where ϵ_k is the final state energy of the spectator electron, f_k is the Fermi function, ϵ_d is the energy of the final two-d-hole state and $V_{kQ}(\omega)$ is the effective matrix element describing the various paths leading to the final state. If one neglects the core hole Coulomb potential, simple second order perturbation theory yields

$$V_0 = \lambda \frac{1}{\omega - \epsilon_a - \epsilon_k} M \qquad (4)$$

where λ is the photon absorption matrix element and M is the Auger matrix element. For simplicity these are both assumed to be momentum independent. The deep core hole energy ϵ_a has the form

$$\epsilon_a = \epsilon_a^0 - i\Gamma \qquad (5)$$

where 2Γ is the Auger decay rate for the core level. In the absence of Coulomb interactions the transition rate is therefore

$$R_Q^0(\omega) = 2\pi |\lambda M|^2 \frac{1}{(\epsilon_Q + \epsilon_d - \epsilon_a)^2 + \Gamma^2} \cdot \rho(\omega - \epsilon_Q - \epsilon_d) \qquad (6)$$

where $\rho(\nu)$ is the conduction band density of empty states. This is just the usual Lorentzion broadened Auger line shape which is so familiar that one may forget how it originates. It is important to recall that this broadening arises because the total energy of the system is shared between the photoelectron and the Auger electron. The uncertainty in how the energy is divided is determined by the lifetime of the intermediate state. This point will be relevant to a determination of the width of the satellite line.

The sudden switching on of the core hole potential produces many body excitations in the conduction band and modifies the effective matrix element of Eq. (4) in a manner similar to the x-ray edge problem (13-15). In that problem the Coulomb potential is turned on at the same instant that the spectator electron is injected into the conduction band. The present problem is more complex since a potential U is switched on initially but this is later changed to U' when the Auger event occurs.

For the limiting case U=0, U'<0 the Auger spectrum is given by

$$R_Q(\omega) = R_Q^0(\omega) \left| \frac{\epsilon_d + \epsilon_Q - \omega}{\epsilon_a - \omega} \right|^{2\rho U'} \qquad (7)$$

which has a power law divergence (U' < 0) similar to that in the x-ray edge problem. Eq. (7) indicates that many body effects greatly enhance the transition amplitude when the spectator electron final energy is near zero (the Fermi energy). Since energy must be conserved overall, this results in a satellite peak on the high kinetic energy side of the Auger line. An alternative point of view is that the potential U' effectively enhances the density of states near the Fermi energy. Eq. (6) then yields two peaks; an Auger peak at $\epsilon_Q = \epsilon_a^0 - \epsilon_d$ where the energy denominator is minimized and a satellite peak at $\epsilon_Q = \omega - \epsilon_d$ where there is a peak in $\rho(\omega - \epsilon_Q - \epsilon_d)$. $R_Q(\omega)$ is displayed in Fig. 4 on a binding energy scale. There is a main Auger peak at constant kinetic energy and a smaller satellite line at constant binding energy. Near the threshold photon energy these merge to form a large resonant peak in the spectrum.

If one thinks of the x-ray edge singularity as being due to an exciton at zero binding energy, it is clear that the present picture should contain features relevant to the discrete exciton induced satellite such as that in GaP (8). One finds that the spectral map of Fig. 4 contains a wealth of information about the general properties of satellites common to several different systems. It is therefore worth considering several points in greater detail.

First one sees that, as noted above, the Auger line is at constant kinetic energy and carries the core hole broadening. The satellite however is narrower and tracks the photon energy. This is because the photoelectron is pinned in the exciton state and energy conservation sharply defines the satellite energy (16). It is as if one is doing a coincidence experiment which constrains the photoelectron energy (17). This effect can be seen in the GaP data (8).

While the core hole width does not affect the satellite width it does control its strength. One sees from Eq. (7) that the satellite strength arises from an enhancement factor multiplying the tail of the Auger Lorentzian strength. This raises another important point illustrating the great generality of Fig. 4. The energy scale is in units of the core hole width since this turns out to be the fundamental energy unit in the problem. One might think that increasing the core hole width could broaden the Auger line enough to destroy the satellite. However, since the satellite strength increases, and its width does not, one can go proportionately further above threshold in photon energy and again resolve the satellite. Hence the core level width scales out of the problem.

Another important point to consider is the comparison which is often made between the photoabsorption (or electron loss) line shape and the satellite line shape (7,8). There is not a simple relationship between these quantities in this model. In the present case the photoabsorption sees the conduction band empty density of states broadened by the core hole width while, as has been shown, the satellite does not carry this width. Furthermore, the values of U and U' affect the photoabsorption and satellite line shapes differently. In particular for U < 0, U'=0 (a situation approximately realized in the LVV Auger transition in simple metals) the photoabsorption exhibits the many body peaking near threshold but there is no satellite at all. Whereas for U = 0, U' < 0 there is a satellite but no peaking in the photoabsorption. Another limiting case U = U' can be treated analytically (12) and is found to give a stronger satellite than Eq. (7). As DF note, this is because the photoabsorption cross section is enhanced at threshold (and has the same shape as the satellite).

The two limiting cases U = 0, U' < 0 and U = U' span the range of reasonable possibilities (for a quasi-atomic system) since one expects 0<|U| < |U'|. It is interesting to note that as far as the conduction electrons are concerned, the case U = 0, U'< 0 may be realized in the rare earths since the 4f level is so localized that the conduction electrons see little or no perturbation if the core excitation is into the 4f level (18).

SUMMARY

I have discussed the general features of the photoemission satellite phenomenon from a unified point of view which shows the necessity of considering the entire process from initial photoabsorption to final generation of the decay products. The main point I wish to emphasize is the role of coherence carried over from initial excitation to final deexcitation and the essential role of incomplete relaxation in the intermediate state.

The particular mechanism of the DF model for satellites in filled d shell metals was analyzed in some detail. The predictions of this model serve as useful illustrations of the general properties of photoemission satellites and the physics behind them.

The picture presented here should be quite generally applicable to any process with localized holes in the final state. Thus in addition to further experimental investigations of photoemission satellites in filled d shell materials, it would be of great interest to look for this phenomenon in other photoinduced core-core-core Auger spectra near threshold.

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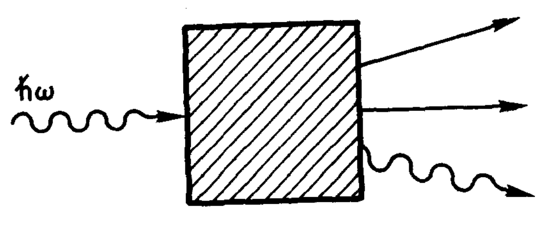

Fig. 1. A black box representing all possible paths between the initial and final states.

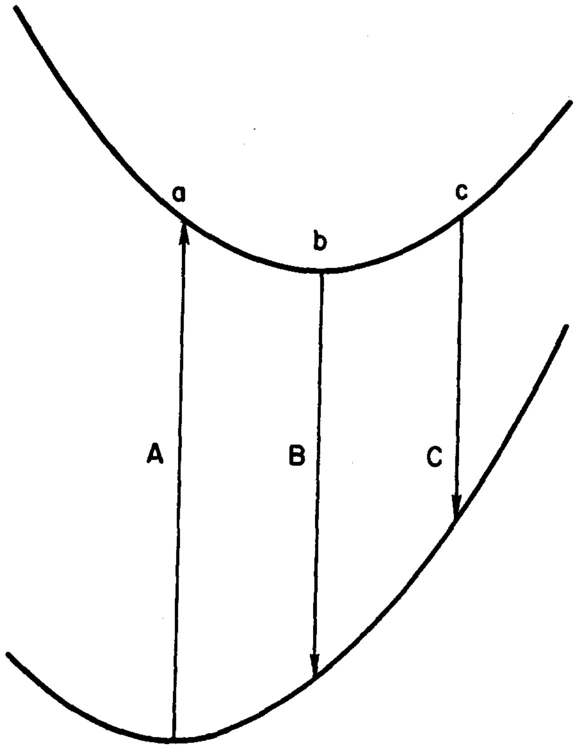

Fig. 2. Configuration coordinate diagram for the x-ray emission problem. The upper and lower curves represent total energy vs. displacement with and without the core hole.

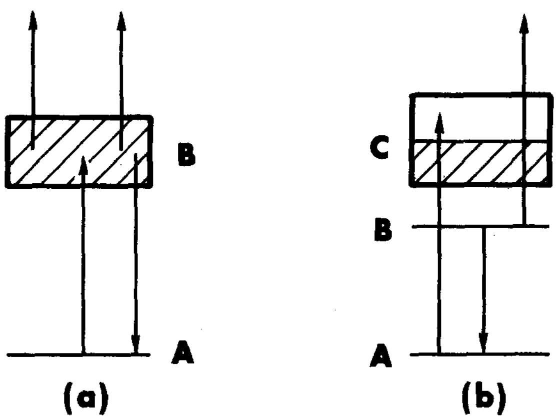

Fig. 3. (a) General level scheme. (b) Level scheme for the DF model. The specific states are described in the text.

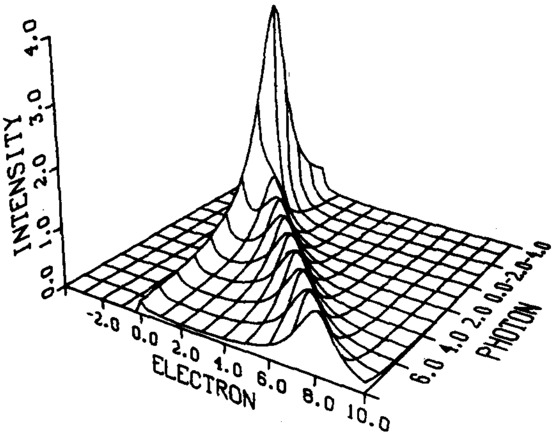

Fig. 4. Calculated Auger spectrum for the case U = 0, U' < 0 plotted vs. photon energy and electron binding energy. The diagonal ridge is the usual Auger spectrum. The ridge at zero binding energy is the satellite. The two merge at threshold (photon energy equal to zero). The figure is in units of the core hole lifetime, Γ and is for the case $\rho U' = -0.3$. A d hole lifetime of 0.1 has been assumed.

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