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Shallow-Deep Instability of Impurities and Core Exciton States in Semiconductors

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The binding energy of core exciton states in semiconductors has received experimental as well as theoretical attention in recent years. One of the reasons of this interest is the discrepancy between the experimental values (0.1 - 0.3 eV) and the theoretical predictions (typically ~0.05 eV) that result from an effective-mass (EM) treatment in analogy to shallow impurities.

We shall discuss the relevance to the core exciton problem of some recent advances in the theory of impurity states in semiconductors with multi-valley band structures, i.e. characterized by the energy degeneracy or near-degeneracy of several band extrema located at different $\vec{k}$-space points. In such cases (e.g. Si, Ge, GaP, some III-V alloys, etc.) resonant or near-resonant intervalley scattering via the large-momentum components of the impurity (or core-hole) potential makes the traditional EM approximation inapplicable. The intervalley contributions to the binding energy are very sensitive to the detailed microscopic structure of the Bloch functions (usually neglected in the EM approach), which must be obtained explicitly by a band-structure calculation. Furthermore, the intervalley terms play a crucial role in determining the binding energy. Depending on their magnitude, they can be a small correction to the EM one-valley values, or can be dominant and make the level deep. It is therefore natural to consider the possibility of explaining the large binding energies reported for core excitons via this multi-valley shallow-deep instability mechanism.

Results are presented, based on empirical pseudopotential band-structure calculations and on a careful treatment of the multi-valley equations which rule out the relevance of this mechanism for Si 2p-core excitations,[1,2] in contrast to recent claims[3] to the contrary. Results on the Ga 3d-core spectra of GaAsP alloys are also discussed. This system is particularly interesting in view of the direct observation[4] of effects of

mixing of X and L conduction band minima via the core-hole potential. The theoretical results for the intervalley matrix elements are too small by about one order of magnitude to explain the observed effects. The implications of this discrepancy for the validity of the analogy between core excitons and donor impurity states is discussed.

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EXCITONS FROM d-CORE LEVELS IN SEMICONDUCTORS

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ABSTRACT

We are concerned here with transitions from shallow (20-40 eV) 3- and 4-d core levels to the L and X lower conduction band minima of semiconductors containing Ga, In, Ge, As, and Sb. Information is obtained by measuring highly precise reflectance spectra, differentiating numerically twice with respect to energy, then following the variations in energy and strength of the resulting structures as a function of temperature, alloy composition, and electric field.

These transitions are interesting because the creation of a localized core hole should be equivalent in some sense to the substitution of a donor impurity at the lattice site (e.g., Ga→Ge). The advantages over many point-defect experiments are that the identity and unit-cell location of the "impurity" are unambiguous, and that lattice relaxation is not important. Yet both self-energy (core-exciton binding energy) and the mixing energies of the L and X minima are substantially larger than effective mass estimates, indicating a strong central-cell component to the core-hole potential.

We shall discuss explicitly:

1. The binding energies of the core excitons. These cannot be measured directly, but estimates from three independent types of experiments consistently show values in the 100-500 meV range, significantly larger than effective-mass estimates. The experiments include (a) direct comparisons between optical and photoemission thresholds; (b) comparisons among L and X thresholds for Ga3d and In4d core levels in mixed-cation crystals; (c) an electroreflectance lineshape analysis of the X_1 structure in GaP.

2. The variation of threshold energies and oscillator strengths of L and X transitions in $GaAs_{1-x}P_x$ and $Al_xGa_{1-x}As$ alloys. The unperturbed L and X minima cross in these series, with L below X in GaAs and X below L at the other endpoints. The data show an anticrossing behavior described by a 2×2 Hamiltonian. This Hamiltonian results from a reduction of the original 7×7 effective-mass Hamiltonian by a valley-orbit splitting of the four L minima accompanied by a mixing of the triplet L levels with their counterpoints at X. Both processes are driven by the core-hole potential. The L-X mixing matrix element is just half the splitting energy at the point of closest approach.

3. Estimation of the relative importance of long-range Coulomb and central-cell effects. An effective-mass transformation shows the final states to have p-like symmetry on a microscopic scale with macroscopic 1s envelopes. L-X mixing follows principally from the central-cell part, while both central-cell and long-range Coulomb interactions participate nearly equally in determining the exciton binding energy.

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THE EFFECT OF DYNAMICAL SCREENING ON THE BROAD FEATURES

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ABSTRACT

Until now, the interpretation of experimental X-ray spectra has been based almost entirely on one-electron band theory. This simple description, which ignores the fact that a strong perturbation due to the presence of the core hole is either switched on (absorption) or off (emission) in the X-ray process, has been remarkably successful especially in the case of emission spectra. This fact led the authors to the Final State Rule [1,2], according to which accurate X-ray spectra of simple metals can be obtained from one-particle theory provided the dipole matrix elements are calculated from one-particle orbitals obtained in the potential of the final state, i.e. in the potential which incorporates the core hole in absorption but not in emission. This rule expresses the success of band theory for emission spectra and is not contradicted by the relatively good agreement between band theory and experiment in the case of absorption spectra since we have shown [3] that the core hole does not have a strong effect on the density of unoccupied states in simple metals. The small effect near threshold due to excitonic enhancement [4] and shake-up suppression [5] can of course not be obtained in this way but can be accurately accounted for by multiplicative singular power law factors [3]. The simplest possible extension of one-particle theory is due to Nozières and de Dominicis (ND) [6]. Their theory, which accounts for the basic dynamics of the X-ray process, namely the switching of the core hole potential, was shown by us to obey the Final State Rule with a high degree of accuracy [2,3,7,8]. Their theory does, however, not account for the interaction between the valence electrons and, given the success of the Final State Rule for the interpretation of experimental spectra, it would be quite interesting to know if the rule would survive the inclusion of the valence-valence interaction. The theory of Nozières and de Dominicis can be generalized to include this interaction in a rather straightforward way. The interaction enters the theory in essentially two ways: (i) the free-electron propagator of ND theory is replaced by the one-particle Green function of the interacting system, and (ii) the static core-hole potential of ND theory is replaced by a dynamically screened potential. We shall present here numerical results for X-ray emission spectra in which a linearly screened potential has been included to infinite order. The results show no further deviation from the Final State Rule. In these calculations a non-interacting valence propagator was used but calculations with an interacting propagator are now being carried out. We do, however, not expect to obtain very different results. There are known to be strong cancellations between dressing up the Green functions and including dynamical screening.

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XANES AND EXAFS: BASIC PROBLEMS AND APPLICATIONS TO LOCAL STRUCTURE DETERMINATIONS OF SURFACES AND COMPLEX SYSTEMS

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The experimental methods to measure surface X-ray absorption spectra using synchrotron radiation will be described. The applications of surface EXAFS and surface XANES, measured by "total yield", "Auger yield", "ion desorption" and "angular integrated constant initial state" techniques, to structural determination of surface chemisorption sites, of clean surfaces and of surface oxide layers will be reported [1].

We shall also report on recent developments of XANES (X-ray Absorption Near Edge Structures) to obtain complementary information, which cannot be obtained by EXAFS, on local structure determination of complex systems [2].

Finally, evidence of the core-hole-induced relaxation effects on the XANES of mixed valence systems has recently been found [3].

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Inner Level Spectroscopy on Layered Crystals*

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The new synchrotron radiation sources have made it possible to investigate with ease inner level x-ray absorption spectra both for atoms in the volume and on surfaces. For example, in recent years extended x-ray absorption fine structure (EXAFS) has developed into a powerful local diffraction technique which is site sensitive. In recent work of our group (B. M. Davies)[1] we have tested EXAFS as applied to a variety of layered crystals including $NbSe_2$, $HfSe_2$, TiS_2, $TiSe_2$, $TiTe_2$, $ZnSe_2$ and $TaSe_2$. Fourier transform analysis using the theoretical amplitude and phase shift information of Teo and Lee[2] was found to give very good first and second neighbor distances (±0.02 A) as compared with x-ray diffraction data. We then applied EXAFS to the Zr K-edge in the adjustable bandgap system $Zr_xTi_{1-x}Se_2$, where control over charge density wave formation has recently been achieved.[3] In this system a zero bandgap alloy is formed at $x \sim 0.15$ intermediate between the semimetal $TiSe_2$ ($Eg \sim -0.2$ eV) and $ZrSe_2$ ($Eg \sim 1.0$ eV). The EXAFS experiments on Zr show that Zr substitutes for Ti and that the first shell of neighbors expands about 5% with little change for second neighbors.

X-ray absorption near edge structure (XANES) was also obtained with high resolution both for inner levels of the metal and chalcogen atoms in the various layered compounds studied. Generally, peaks in the XANES structure for the metal $NbSe_2$ and for $TiSe_2$ and TiS_2 can be closely coordinated with known density of states. On the other hand, matrix element, atomic, core exciton and other effects are known to be important near threshold. The L_3 threshold of Hf in $HfSe_2$ shows a very strong inner-well resonances or white line. A clear understanding of XANES structure for molecules and solids is just beginning to emerge. In some cases near edge structure is very sensitive to polarization as well as to the nature of the local bond.

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SINGLE AND DOUBLE EXCITATION AND IONISATION FROM p AND d CORE SHELLS OF ATOMS

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Over a number of years, atomic absorption spectra of many elements have been studied between 6 and 600 electron-volts using synchrotron spectroscopy. Most of the data relates to energy levels, with some information also on relative intensities and shape resonances in the continuum. From this vast quantity of data, a picture emerges of how profoundly core level excitation in atoms differs from the single excitation of outer electrons. Selected examples will be given covering aspects such as centrifugal barrier phenomena, double excitations and interchannel interactions. Results on the d to f shape resonances for the lanthanide and actinide sequences will be compared. Evidence for double ionisation and two step autoionisation from absorption studies will be presented. An attempt will be made to relate this evidence to recent experimental work by other authors on the direct measurement of double ionisation rates.

INNER SHELL EXCITATIONS IN HEAVY ATOMS

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Electrostatic effects are highly predominant in inner electron binding energies. Besides, there are important relativistic and quantum electro-dynamical (QED) corrections necessary for the inner shell excitations. Using the relativistic density functional theory an appropriate one electron potential is constructed (1). The QED effects are contained self-consistently in it in a local density approximation (LDA). Results are presented for (a) K-shell binding energies for all closed shell high Z atoms (b) K-α hyper satellite energies for Tm,Hg and Tl. These LDA results are compared with the nonlocal Dirac-Fock calculations and experimentally determined energies. The discrepancies are discussed in terms of further many-body effects.

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3p→3d Excitations in Transition Metal Atoms and Solids

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Photoabsorption and photoemission in the region of the 3p threshold (30-100eV) of the 3d transition metals will be discussed. The interpretation of experiments and their implications for electronic structure will be given first for atoms and then for solids.

In these atoms, the 3p→3d dipole matrix elements are large. Approximately half of the total one-electron oscillator strength for 3p→nd,ϵd is contained in n=3. The large peaks observed in absorption measurements [1] correspond to the excitation of $3p^5 3d^{n+1} 4s^2$ states from a $3p^6 3d^n 4s^2$ ground state. Since the energy of the excited states is well above the $3p^6 3d^{n-1} 4s^2$ threshold, autoionization is energetically possible. The decay matrix elements are the same as for super-Coster-Kronig (sCK) processes and typically give widths ~1-2eV. This is not so large as to wipe out the 3p core level, but does give rise to interesting effects. Interference between the two-step process described above ($3p^6 3d^n 4s^2 \rightarrow 3p^5 3d^{n+1} 4s^2 \rightarrow 3p^6 3d^{n-1} 4s^2 \epsilon f$) and the direct excitation of $3p^6 3d^{n-1} 4s^2 \epsilon f$ continua results in Fano line shapes [2]. The interpretation in terms of sCK transitions is conclusively proved by the observation of sharp structure due to unique decay selection rules; e.g. in Mn, decay of $3p^5 3d^6 4s^2 (^6D)$ to $3p^6 3d^4 4s^2 \epsilon f$ is forbidden by symmetry [3]. Experimentally [4], these states are much narrower than the (^6P) states which are allowed to decay.

Since the 3d subshell is full in Cu, the 3p absorption is much weaker, the lowest lines being due to $3p^5 3d^{10} 4s^2 (^2P)$. These states can readily decay via sCK to $3p^6 3d^8 4s^2 \epsilon f$. However, their direct excitation is extremely weak, being a two-electron transition, and the 3p→4s peaks are nearly symmetric. It appears that some interference occurs in higher energy transitions involving $3p^6 3d^{10}$ 4snd and ϵd states.

So far no photoemission experiments have been reported for 3d metals in the vapor phase, but recently measurements have been done for Cu [5]. The strongest emission is from the Cu^+ $3d^9 4s (^{1,3}D)$ final states. A resonance in the $3d^8 4s^2$ (primarily ^1G) states at the 3p→4s energy is observed which is due to the sCK processes described above. These experiments provide further confirmation of the general picture presented here.

For solids, the interpretation of absorption measurements [6] is much the same as for atoms except for the complications introduced by the band nature of the 3d levels. Ni is the most atomic-like and is probably the best understood. Here the empty portion of the 3d bands is so narrow that the resonance in absorption appears approximately as a simple Fano line shape. The closest atomic equivalent is $3p^6 3d^9 \rightarrow 3p^5 3d^{10}$. In fact, due to 3d band screening, the $3p^5 3d^{10}$ configuration describes the local charge distribution in the presence of the core hole rather well. The sCK decay of the excited state is predominately to a localized $3d^8$ excitation, i.e., two 3d holes bound on the same atomic site. These states correspond to the 6 eV satellite which undergoes a resonance at the 3p excitation energy [7]. Since the direct (non-resonant) excitation of the 6 eV satellite is not very strong, the resonance is not strongly asymmetric. Most of the interference occurs in the valence band emission due to solid state processes which involve extended 3d states.

For the rest of the 3d transition metals, atomic effects are not prominent. Nevertheless, interference effects are observed in both absorption and photoemission; localized excitations are not necessary. Following excitation of the 3p electron into 3d states above E_F, two types of sCK decay can occur in a strictly band model. The first is coherent with photoemission from the 3d valence bands and causes interference. The second process is incoherent, since it results in two 3d holes below E_F and an excited electron above E_F. In the absence of strong d-d replusion, the kinetic-energy distributions of the emitted electrons partially overlap for the two processes.

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CORE-LEVEL SPECTROSCOPY IN MIXED VALENCE MATERIALS

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ABSTRACT

The photoionization of an inner shell electron causes a relaxation rearrangement of the outer electrons in the atom. We investigate the consequences of this rearrangement for solids in a mixed-valent state, on the resulting photoemission spectrum. The ground state degeneracy between states of different valency is broken by the core hole potential. The two main final state peaks in the core hole spectrum are shown to have a relative weight which does not correspond directly to the initial state mixing.

Effects of the environment on core excitons

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The theory of Frenkel core excitons in semiconductors [1] will be reviewed. Such excitons have energies determined primarily by the static central-cell potential of the core hole, rather than by the long-ranged part of the electron-hole interaction. They are to be contrasted with ordinary Frenkel excitons which are atomic-like, because they are anti-bonding host-like states; and they differ from, but coexist with, Wannier excitons.

The energies of these Frenkel excitons can be computed using the optical alchemy approximation [2], which treats a core-excited atom of charge Z as an "impurity" of charge Z + 1; thus excited Ga is "Ge." Hence judicious use of the theory of deep impurities [3] permits us to predict Frenkel core exciton energies in the bulk [1] and at surfaces [4] or interfaces [5].

With this approach, we have a unified view of synchrotron radiation data, Schottky barrier heights [6], and surface states [7].

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Abstract for the Symposium on Core Level Excitations in Atoms, Molecules and Solids, International Centre for Theoretical Physics, Trieste, Italy, June 22-26, 1981.

ATOMIC ASPECTS OF CORE-LEVEL SPECTROSCOPY*

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The spectroscopy of atomic core vacancies appears to be in a mature state of development with regard to the classification, measurement and calculation of energy levels as well as to the approximate determination of photoabsorption and Auger probabilities. It is instead in its infancy with regard to the correlation effects that result from the interaction of any core vacancy with its environment. Advancing the study of these correlations in atoms acquires a high priority as a prerequisite for the corresponding study of molecules and condensed media, which looms very significant owing to its greater range of phenomena and applications.

Most conspicuous among correlation effects is the relaxation of the outer atomic shells about inner shell vacancies acting as positive "holes". The energy import of this relaxation amounts to 5–10 eV and is thus amply sufficient to upset the valence shell structure and dynamics. An outline of the fragmentary but basic information on atomic relaxation has been given in a recent thesis.[1] Correlations may also cause a vacancy to transform into two or more vacancies, typically through Super-Coster-Kronig transitions; the theoretical analysis of this phenomenon has been pioneered by Wendin[2] and Cederbaum.[3]

Relaxation manifests itself instructively through the side effects of core vacancy formation, particularly through the dependence of such effects on the available energy. When the energy barely suffices to eject an electron from a core level, relaxation must run its course and release its energy before the electron leaves the atom. In the opposite limit the core electron receives excess energy from an external source and escapes swiftly; the relaxation energy is then distributed between the ejected electron and the outer shells in the "shake-up" process. These circumstances have long been familiar, but the evolution of the ejection process from one limit to the other does not appear to have been documented extensively by experiments, in contrast to the study of each limit.

Since relaxation involves a large number of outer shell particles its correlation with the motion of the ejected electron will have to be described in terms of collective coordinates. Clues to such a treatment may be drawn from the treatment of photoionization of the valence shell. Indeed photoionization leads to relaxation of the residual ion and to a significant rate of its excitation regardless of whether it acts initially on a valence or core electron. The treatment of outer shell ionization by appropriate – if unfamiliar – coordinates provides now at least a semi-quantitative description of the entire evolution between the limits of slow and fast electron ejection.[4] The relevance of this approach – and of its conceivable extensions[5] – for the formation of core vacancies will be discussed.

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CONDUCTION ELECTRON RESPONSE TO CORE EXCITATIONS IN METALS.

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It has been recognized since the early work of Friedel that core excitations in metals differ from those in insulators by the fact that metallic conduction ensures that the core hole must be fully screened by the conduction electron response, provided only that the core hole lives longer than the plasmon period. This response has two important effects. First, the energy of the system is modified by the conduction band distortion and the threshold for the core excitation is, accordingly, shifted. Second, the conduction electron response provides a mechanism for energy absorption by creation of quasiparticle pairs in the band. Core lines are thereby broadened into edges with shapes characteristic of the core hole - conduction band coupling. The work reported here concerns both the threshold energies and the absorption profiles that are observed in various cases chosen for ease of interpretation.

It can be stated that the edge shifts observed in practice are well--understood in principle and are, in a number of cases, predictable to within ~ 0.2 eV. The remaining difficulty is the usual one that chemical energies involving differences between two configurations of solids often cannot be calculated by a priori methods to much better than 1 eV, which unfortunately is the order of magnitude of the observed shifts themselves. Chemical parametrizations of the energy changes may be as much as an order of magnitude more accurate than can readily be achieved by a priori calculations. We show here for a variety of examples that the core edge energies can be reproduced to within a few tenths of 1 eV by the "Z + 1 analogy" together with estimates of the Stokes shift having comparable accuracy. We conclude that a generally satisfactory understanding of threshold energies is available.

The situation is quite different for the thereshold profile. Systematic qualitative changes in thereshold profile are observed for which even schematic theoretical understanding is currently lacking. It had formerly been believed that a semiquantitative understanding of threshold processes was available for the fairly sharp edge structures observed for the outer core excitations of pure alkali metals, Mg and Al. The work reported here makes direct contact with these earlier results by probing the electronic systems of these same metals using foreign atom probes. Two sets of results are discussed as follows.

When chemically simple foreign atoms are introduced into alkali metals host lattices their excitation profiles are found to be strongly characteristic of the impurity chemistry and quite different from those of other chemical species. Thus different rare gases have similar profiles, as do the halogens, but the halogens differ strikingly from the rare gases and neither resembles the host alkali sharp edge structure. Instead, the rare gases exhibit a linearly increasing absorption, while the halogens have a gaussian step consistent with a phonon broadening which agrees with the Stokes shift. In all cases the threshold energy is well understood but the profile remains an enigma.

In a second, equally revealing, series of experiments, alkali metal adsorbates have been deposited on clean host surfaces of Cs, Rb, K, Na, Li and Mg. Cs adsorbates, when sprinkled at dilution on these surfaces, exhibit a thereshold structure which increases fairly slowly to a sharp peak on the heavy alkali substrates, but the peak broadens on Na and Li, finally giving rise on Mg to a linear threshold almost identical with that of rare gas impurities in alkali metals. The profile changes fairly systematically as the host electron liquid increases in density from Cs to Mg. Arguments to be presented suggest that the linear profile is characteristic of strong coupling between the conduction band and the excited center, while the sharp peaks appear as "white lines" when the excited levels decouple from the bottom of the host conduction bands.

With any of these substrates, the dilute adsorbate limit is achieved at surface densities of about 10^{14} cm^{-2}. As the density of Cs is increased to ~ 10^{15} cm^{-2} (ie about one monolayer) the spectrum acquires major features recognizably characteristic of pure bulk Cs, including the sharp edge structure. The sharp edge is thus characteristic of Cs atoms interacting among themselves, even in planar layers, and not of Cs interacting with an electron liquid in general. Spectra for Rb on other alkali metals resemble those discussed above for Cs but are generally more sharply peaked.

We conclude that the chemistry of the ground and excited configurations of centers interacting with metal hosts are, in many cases, quite well understood. The effect of host-core coupling in modifying the excitation spectrum through electron-hole pair creation remains almost entirely unpredictable.

Extended Abstract/not for publication

LINE SHAPES IN CORE ELECTRON SPECTROSCOPY

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This talk will concentrate on discrete core level satellites in XPS arising from localized screening processes (as opposed to plasmon satellites). It is convenient to divide the satellites discussed into two groups although they have much physics in common.

First, Ni and Pd XPS spectra show core level satellites with ~ 6 eV higher B.E. than the main peaks. The satellites are, of course, attributed to final states in which a d hole in the valence band is correlated with the core hole (d^9 final states).

The main (best screened) peak is attributed to transitions to final states with a full valence d shell at the site of the core hole. We have investigated about 50 intermetallic compounds and alloys of Ni and Pd. The satellites are consistently weaker when the partner element is less electronegative than Ni or Pd and more intense in alloys with more electronegative elements. The trends in XPS valence band satellites are similar, and at the same time the density of Ni or Pd d states at the Fermi level decreases. For 1 : 1 Ni alloys the core level satellite intensity varies almost linearly with Pauling electronegativity, but is less well correlated with Miedemas electronegativity, the heats of formation of Ni alloys, and calculated chemical potentials of electron affinities in the pure partner elements.

A naive model relating satellite intensity to the number of holes in the Ni or Pd d bands does qualitatively explain the variations of satellite intensity. However calculations which take into account the changes in density of states at E_F might well show this model to be inadequate.

A second group of satellites occurs in core level spectra of the early rare earths and actinides due to different occupation of the valence f levels in the presence of a core hole in the final states. For instance in intermetallic Ce compounds three sets of 3d XPS peaks are found corresponding to final states with 0, 1 and 2 4f electrons on the core ionized atom. There is a strong tendency for the "$4f^0$" and "$4f^2$" peaks to grow at the expense of "$4f^1$" peaks as the electronegativity of the partner element is increase in Ce compounds.Related trends are found in other early rare earth and actinide compounds.

In view of the difficulties involved in obtaining direct information on the nature of the 4f levels in Ce it is sensible to try to deduce some of the properties of these levels from core level line shapes. The effects seen in XPS and X-ray adsorption are at least in part, simulated by the Toyozawa - Kotani / Schönhammer - Gunnarson model calculations if we assume that the Ce 4f levels are more strongly coupled to other valence levels in Ce compounds with electronegative elements. It doesn't seem necessary to invoke ideas of "mixed valence" to explain core level XPS and X-ray absorption results of Ce and its compounds.

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[*] Experimental work done in cooperation with P. Bennett, M. Campagna, U. Hillebrecht, R. Lässer and Z. Zolnierek.

Time-dependent Phenomena in Core Level Excitation

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In Auger electron spectroscopy (AES) a core hole is created by photons or electrons and its decay via an Auger process is studied. By the creation of the core hole the valence electron system may also be excited locally. In extended systems the excitations can decay and (or) propagate away and if the core hole life-time is long the probability that an excitation will influence the Auger decay is small. A two-step approximation is therefore usually introduced by assuming that the valence electron system has locally relaxed to the new ground state when the Auger decay occurs. For core hole life-times comparable to the time scale of the relaxation processes such a two step approximation breaks down, because the Auger electron can pick up the excitation energy created in the XPS process. This effect requires a theoretical description in which the creation of the core hole and the Auger decay are treated as <u>one</u> process.

We have developed such a one-step description[1] based on the quadratic response formalism. The electron current is calculated to lowest order in the external field and it is assumed that the emitted electrons have a large kinetic energy so that the sudden approximation can be used. The behaviour of the centre of gravity of the Auger spectrum shows very nicely the two time scales involved. For an XYZ spectrum, for instance, there is a term which depends on the X-hole life time $1/\Gamma$,

$$\sim \int_0^\infty V(t)\, 2\Gamma\, e^{-2\Gamma t}\, dt \quad ,$$

where V(t) describes the time dependent change of the electrostatic potential at the core holes after the X hole has been created. The centre of gravity depends sensitively on whether the decay or screening process is faster.

In free-electron like metals plasmons are excited in the XPS process and the Auger electron can therefore pick up the plasmon energy in a plasmon gain process. We have calculated the probability that such a process is observed a time t after the core hole was created[2]. For times that are not too short interference effects between different gain events lead to a nonexponential behaviour $e^{-2\Gamma t}/t$. This corresponds to a non-Lorentzian energy distribution

$$j(\varepsilon) \sim \frac{\Gamma}{\sqrt{(\varepsilon-\omega_p)^2+\Gamma^2}}$$

close to the plasmon gain peak. Interference effects between gain and no gain events also lead to important effects on the line shape.

It has recently been demonstrated that AES and XPS can be performed in a coincidence experiment (APECS), where the Auger spectrum $j(\varepsilon_p,\varepsilon_k)$ is measured for a given energy ε_p of the XPS electron. If the system has insufficient time to relax before the Auger event, APECS can give more information than separate XPS and AES experiments. For a finite system, for instance, we can study an XYV process involving a valence level $|a>$. For a given XPS energy ε_p , the ratio of the total Auger current from this process and the corresponding XPS current is proportional to

$$< E_n^{N-1} | n_a | E_n^{N-1} > ,$$

where $|E_n^{N-1}>$ is an excited state corresponding to the XPS energy ε_p. By varying ε_p we can study the relative occupancy $< n_a >$ of the level $|a>$ in the states $|E_n^{N-1}>$. Thus APECS can give information about the spatial character of the excited states[3].

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Energy Shifts of Core Levels from Atoms to Solids

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A general treatment of core level binding-energy shifts in metals relative to the free atom is introduced and applied to all elemental metals in the Periodic Table.[1] The crucial ingredients of the theoretical description are a) the assumption of a fully screened final state in the metallic case and b) the (Z+1) approximation for the screening valence charge distribution around the core-ionized site. The combination of the complete screening picture and the (Z+1) approximation makes it possible to introduce a Born-Haber cycle which connects the initial state with the final state of the core-ionization process.[2] From this cycle it becomes evident that the main contributions to the core-level shift are the cohesive energy difference between the (Z+1) and Z metal and an appropriate ionization energy of the (Z+1) atom. The appearance of the ionization potential in the shift originates from the assumption of a charge-neutral final state, while the contribution from the cohesive energies essentially describes the change of bonding properties between the initial and final state of the site. The calculated shifts show very good agreement with available experimental values (at present, for 20 elements). For the other elements we have made an effort to combine experimental ionization potentials with theoretical calculations in order to obtain accurate estimates of some of the atomic core-level binding energies. Such energies together with measured metallic binding energies give "pseudo-experimental" shifts for many elements. Our calculated core-level shifts agree exceedingly well also with these data.

The treatment of the core-level shift for bulk metallic atoms can easily be generalized to surface atoms. From an empirical relation for the surface energy a simple expression for the shift of the surface core-level relative to the bulk can be derived. For the earlier transition metals, it is found that the core electrons are more bound at the surface than in the bulk, while for the later ones the opposite situation exists. This change of sign of the surface shift depends on the bonding-antibonding division of the d band, and has recently been confirmed experimentally in the 5d series.[3] The surface core-level energy shift can also be interpreted as the surface heat of segregation for a (Z+1) substitutional impurity in the Z metal.[1,4]

The chemical shift of the Z component in an $Z_x(Z+1)_{1-x}$ alloy can be directly related to the partial heat of solution of a (Z+1) metallic atom in the alloy. Thus measured chemical shifts can be used to obtain the heat of formation of the alloy. This has recently been done for the Pd_xAg_{1-x} alloy[5] and has also been applied to more general types of alloys[6,7] (ESCA-calorimetry).

The thermochemical method for the core-level shifts can easily be generalized to the case of Auger electron energy shifts between the free atom and the metal. Also here one finds a good agreement between calculated and measured shifts.[8-10] Also the chemical shift of the Auger energy in alloys can be utilized to obtain thermochemical data.[6]

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EELS studies of 3d excitations in Ba, La and Ce

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Abstract

Electron energy loss spectra of barium, lanthanum and cerium in the regions of 3d level excitations have been found to show doublet structures associated with each 3d spin orbit component. The relative intensities of these structures vary systematically with excitation energy. In each case one component can be associated with a $3d^{10}4f^{n} \rightarrow 3d^{9}4f^{n+1}$ excitation through comparison with photoabsorption and appearance potential spectra. This component dominates the spectrum at high ecxitation threshold. The second component, which appears at 2-3 eV lower energy, dominates the energy loss spectrum at excitation energies within about 200 eV of threshold. For the explanation of this component we propose a process, which involves excitation and decay of an intermediate screened $3d^{9}4f^{n+2}$ state, and which involves concepts like dynamic screening, shake-up and incomplete relaxation.

Core Spectroscopy of Organic Molecules and Crystals[*]

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Absorption, x-ray emission and photoelectron spectra from organic molecules and molecular crystals have been studied for quite some time (e.g. 1, 2, 3, 4). These spectra show a number of interesting features, which are of instrumental importance for an understanding of the electronic structure of these materials. Several general features of these spectra will be briefly summarized by discussing a few specific examples:

Process	Examples
a) inner shell (1s → Rydberg excitations) }	alkenes
b) inner shell (1s → valence excitations) }	fluoromethanes
	benzene
c) valence → K soft x-ray emission	aromatic hydrocarbons
d) the problem of absolute absorption cross-sections	photoresists for lithography
e) near edge structure in organo-metallic compounds	phthalocyanines
f) EXAFS structure	fluorobenzenes (?) biological materials
g) photoemission from organometallic compounds	ferrocene 3d-phthalocyanines
h) resonant outer core/valence satellite structure in photoemisson	3d-phthalocyanines 3d metals

Recent experiments concerning shake-up satellite structure in core level spectra from organometallic compounds (Ni-, Cu-, and Zn-phthalocyanine (PC)) will be discussed in detail (see as examples Figs. 1-3). Prominent $2p_{1/2}$ and $2p_{3/2}$ satellites, which show a complex multiplet pattern, have been observed for CuPC while the satellites in NiPC and ZnPC are only weak (5). The nature of these satellites is discussed by comparison with the pure metal 2p-spectra and in view or recent results from cluster calculations on Metal-Nitrogen (MN_4) systems (6). It is concluded that the valence orbital structure, which was determined independently in photoemission experiments using synchrotron radiation, influences strongly the intensity of satellites and offers a simple explanation for the characteristic change in the 2p-core level photoemission spectra(Fig.4).

Finally recent results for resonant photoemission from organometallic compounds will be presented (7). The observed atomic multiplet structure of the satellites will be discussed. In favorable cases, it can be used to infer the groundstate configuration of the metal in these compounds.

[*] Abstract prepared for the "Trieste Symposium on Core Level Excitations in Atoms, Molecules and Solids" - 22-26 June 1981.

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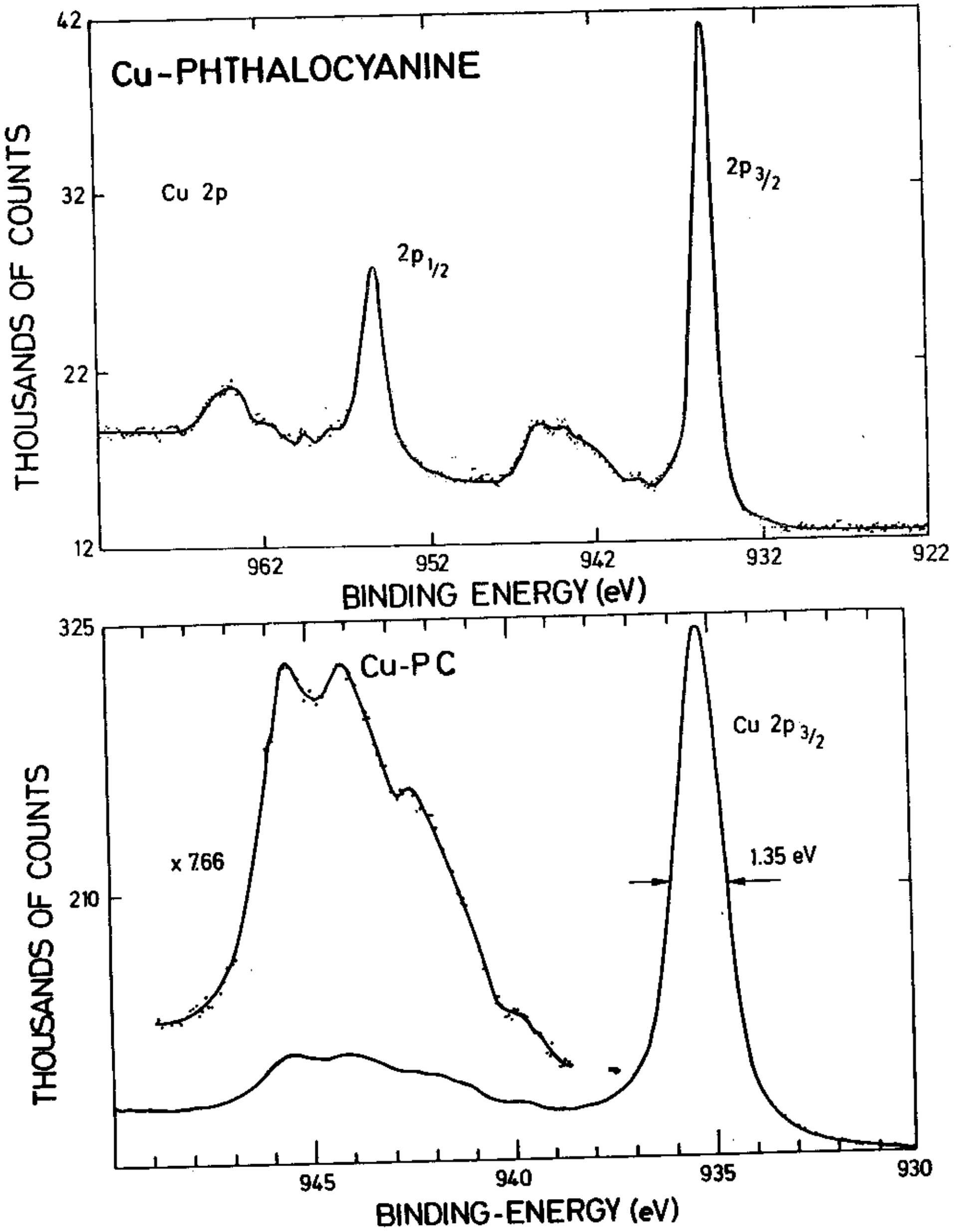

Fig. 1 2p - XPS spectrum of Cu-phthalocyanine taken with monochromatized Al Kα radiation (hν = 1487 eV). The satellite peaks associated with the 2p 1/2 and 2p 3/2 main line are clearly seen. In the lower panel the structure of the 2p 3/2 satellite is displayed on an enlarged scale (from Ref. 5).

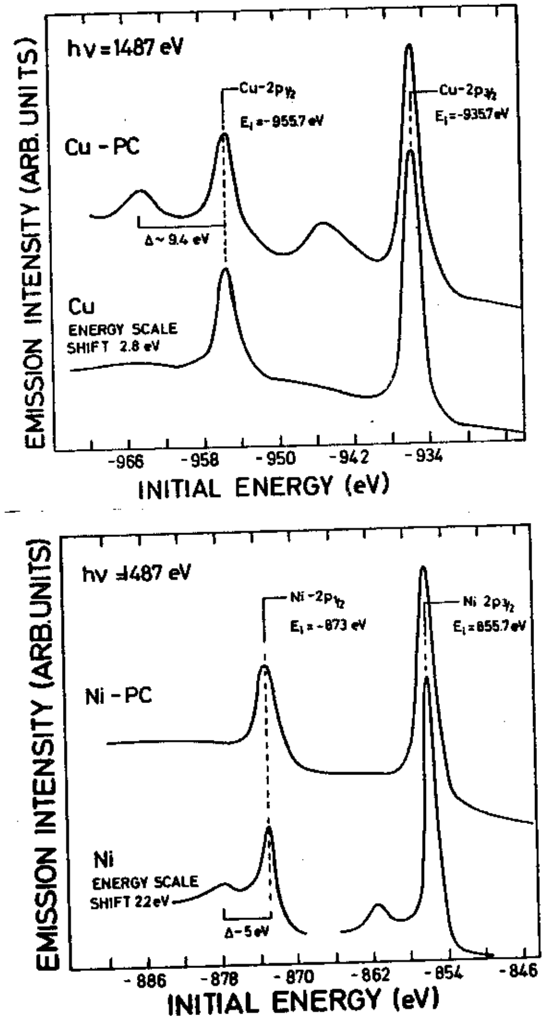

Fig. 2 Comparison of the 2p core level XPS spectra of Cu, Ni, CuPC and NiPC (unmonochromatized Al Kα radiation; the Al K α_3 contribution has been removed by a deconvolution procedure). The energy scales have been aligned at the 2p $_{1/2}$ level.

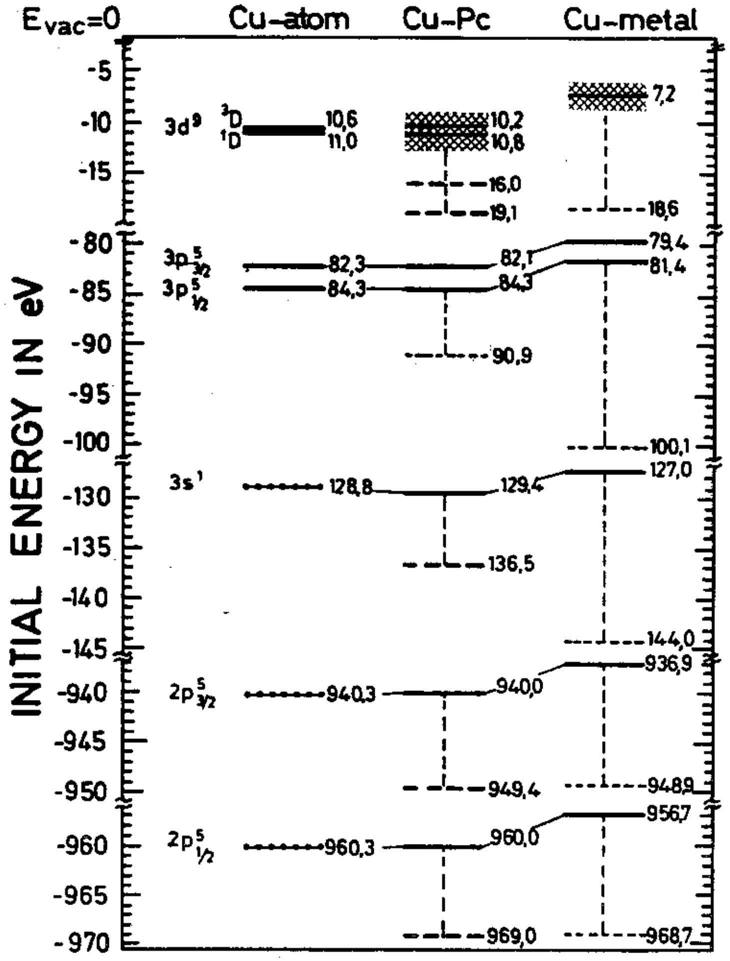

Fig. 3 Orbital scheme of atomic Cu, Cu-PC and Cu metal as derived from UPS and XPS experiments. Solid bars represent main lines, dashed bars denote satellite structures. The binding energies for Cu-atom (dotted bars) have been derived from optical data (from R. Engelhardt, Diplomarbeit, in preparation).

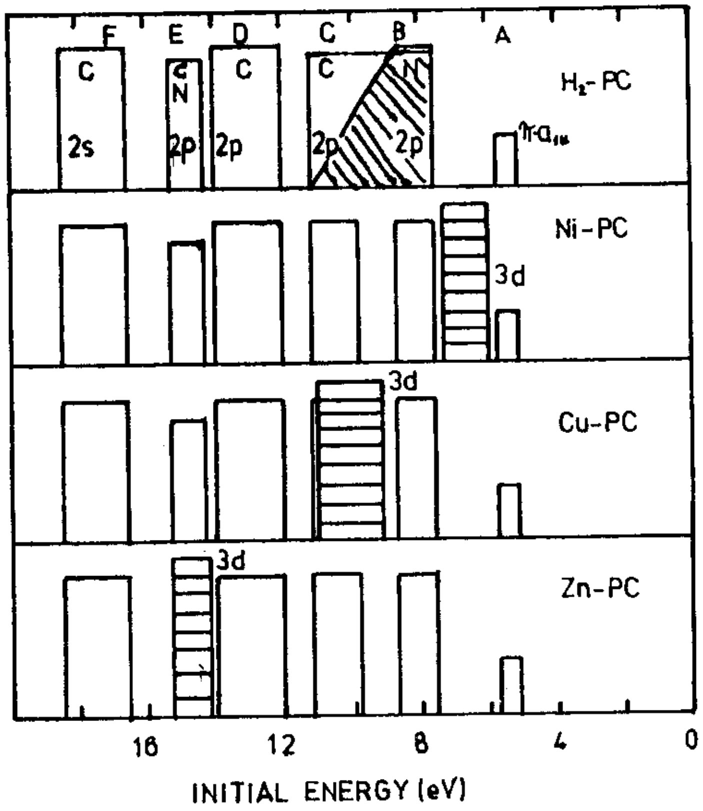

Fig. 4 Schematic representation of the valence orbital structure for 3d metal phthalocyanines as derived from soft x-ray emission and photoemission experiments. Note that for Cu-PC there is a complete overlap of the 3d orbitals with the uppermost N 2p orbitals of the nitrogen atoms surrounding the central metal (from E. E. Koch and M. Iwan, Europhyiscs Conf. Abstract, Vol. 5A, part I, p. 302 (1981), Heidelberg 1981).

SURFACE CORE LEVELS

by
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Due to their reduced coordination number, surface atoms experience a different potential than bulk atoms. So the binding energy of core electrons is modified by the presence of a surface.

Recently surface shifts have been observed for 4f core levels of gold, tungsten, tantalum and iridium (1,2,3). A model is presented, limited to the d series, in which this shift follows the displacement of the center of the local density of valence d states at the surface (4). This model predicts a change of sign of the surface shift near the middle of the d series (i.e. between Ta an W in the 5d series). This was observed for Ta (111) (5).

In the case of oxygen adsorption on transition metal surface, there is a small electron transfer towards oxygen, which leads to a displacement of the d band to larger binding energies, followed by the core levels. For oxygen adsorption on w (110) such shifts were observed in fair agreement with the theoretical model (6). Moreover this interpretation allows to assign a given core level peak to a given site location, which generalizes the possibilities of ESCA to surface geometry determination. Finally new results will be presented on the 4f level shifts of the (100) face of tungsten.

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Plasmon Effects in Core-Level Photoemission

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Abstract

Photoemission, using synchrotron radiation in the photon energy range 100 to to 600 eV, has been utilized to study the energy dependence of the bulk plasmon loss intensity in Si and Al. The results are compared to the predictions of various extrinsic and intrinsic loss models for plasmon creation.

Much attention has been given to the magnitude of the plasmon loss processes[1,2] that photoelectrons can suffer in the excitation event[3] (intrinsic processes) or in inelastic scattering events[4] on their path out of the material (extrinsic effects). These two mechanisms give rise to loss structures that coincide in a photoelectron spectrum so they are not readily separated experimentally. The probability for electron-plasmon scattering in free electron like materials is relatively high[5] for almost any electron kinetic energy, which means that extrinsic effects should always be of importance for such materials. Analysis[6,7] of plasmon loss structure in XPS spectra from Al and Mg indicate that extrinsic effects contribute the major part at those energies. In addition to the extrinsic and intrinsic bulk plasmon losses, the photoelectrons can also suffer losses specific to the surface:[8] surface plasmon losses. Interference[9] between surface and bulk processes may also occur which further complicates the picture.

The samples selected for the studies reported here are Si and Al which have experimentally determined bulk plasmon energies of, respectively, 16.7 eV[11] and 15.7 eV.[2,12,13] These values are close to their calculated free electron plasmon energies. They have thus free electron densities which are nearly equal and should consequently exhibit very similar trends[5] in the loss intensity with kinetic energy. We have studied the loss intensity over as broad a range as was practically feasible. The experiments were performed on the 4° line[14] of Beam Line I at the Stanford Synchrotron Radiation Laboratory. Monochromatized radiation in the photon energy range 100 to 600 eV was used for excitation. Binding energies of 99 eV (Si 2p) and 73 eV (Al 2p) were used when assessing kinetic energies above the Fermi level for the analyzed electrons. A simple graphical deconvolution technique was used in extracting the intensity of the bulk plasmon loss structure from the background of inelastically scattered electrons.

Recordings of the Si 2p doublet and the first bulk plasmon loss structure (labelled P_1) are shown in Fig. 1 for four different photon energies. The parameter to be extracted from the data is primarily the ratio in intensity between the bulk loss structure and the elastic 2p photoelectron peak at the various photon energies used. In order to do that, the area of, respectively, the loss structure and the elastic peak need to be determined which means that an assumption about the proper background to be subtracted must be made. A smoothly varying background is assumed which is illustrated by the dashed lines in Fig. 1.

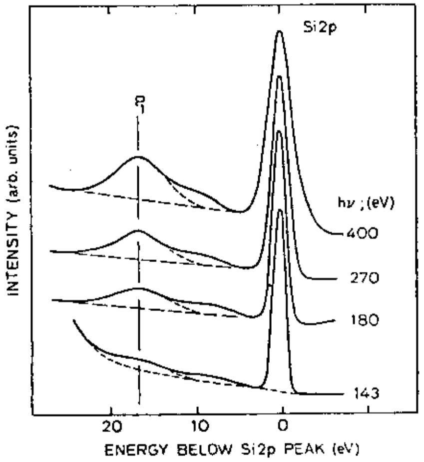

Fig. 1. Photoemission spectra for four different photon energies of the Si 2p spectral region. The first bulk plasmon loss structure is labeled P_1.

The experimental results for the normalized bulk plasmon loss intensity (the peak area ratio) are shown in Fig. 2 as curves (c) and (d) for Si and Al, respectively. The trends of the curves are, as seen, very similar. The normalized bulk loss intensity increases rapidly with electron kinetic energy from the onset and up to 80 to 100 eV kinetic energy. It levels off thereafter and shows a much slower increase. The data has been corrected for the variation in analyzer efficiency with kinetic energy. It is essential that this correction factor is included because it varies significantly, especially close to threshold. The bars on the experimental data illustrates an estimated uncertainity in the area ratio determination

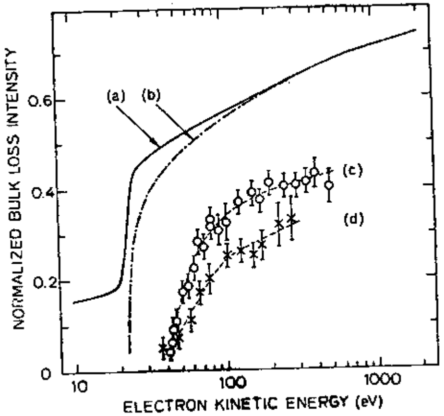

Fig. 2. Calculated (a), (b) and experimental (c), (d) values for the normalized bulk loss intensity, as a function of electron kinetic energy above the Fermi level. Curve (c) represents data on Si and curve (d) data on Al. The calculated curves are based on Tung and Ritchie's[5] calculated electron mean free paths for Al.

Curves (a) and (b) in Fig. 2 represent calculated values of the normalized bulk loss intensity for extrinsic plasmon creation. The model by Mahan[15] of random spatial emission for bulk extrinsic plasmons,[6,12] predicts for a thick sample a normalized intensity of

$$\frac{P_1}{P_0} = \left(1 + \frac{\ell}{L}\right)^{-1}$$

where ℓ is the mean free path for plasmon emission and L is the mean free path for other processes (single particle excitations). Using the mean free path values calculated for Al by Tung and Ritchie,[5] in the case of no damping, curve (b) in Fig. 2 is obtained. Curve (a) gives the values when plasmon damping effects are taken into account.[5]

In a comparison between the calculated and experimental results, one notices two major differences. The absolute values do not agree, which is not surprising, however. Secondly, and of considerable interest, is that there is a discrepancy in the onset energy between the calculated and experimental results. The onset energy extracted from the experimental results by extrapolation falls at 10 to 20 eV higher energy than the theory predicts.

Since the absolute value obtained for the normalized intensity depends on details of the analyzing geometry and plasmon damping effects, among other things already mentioned, we feel justified to rescale the curves (a) and (b) at 300 eV kinetic energy, we obtain the result shown on a linear energy plot in Fig. 3. The trend in the Si data for energies larger than about 150 eV is seen to closely follow the calculated curve. Also, for Al the trend seems to be about the same although we did not cover as wide an energy range in this case and the uncertainty in the data is larger. For energies below 150 eV, the experimental curves are seen to fall off faster with decreasing energy than the calculated curves and the discrepancy in onset energies between experimental and calculated values is again displayed.

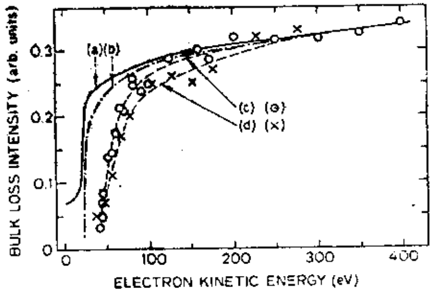

Fig. 3. General shape of the bulk loss intensity as a function of electron kinetic energy above the Fermi level. The curves are those shown in Fig. 2, but they are rescaled to coincide at 300 eV electron kinetic energy.

For the moment, we have no unambiguous interpretation of the observed faster decrease of the loss intensity with decreasing kinetic energy and of the higher onset energy than predicted by the extrinsic model. It may be caused by the proposed interference effects[9,18] due to influence of the surface and hole plasmon coupling. However, it should be noticed that our results indicate that these effects seem to be of relatively little importance at kinetic energies above 150 to 200 eV. One possible interpretation of the observed discrepancy would be to claim that the calculated mean free path values have to be adjusted. A systematic study of the bulk loss intensity close to threshold for materials with different free-electron densities would be of great importance to clarify the existing discrepancy between experiment and theory. Specific suggestions of such experiments will be discussed as well as possible developments of existing theories.

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ANALYTICAL SOLUTION TO THE MND EQUATIONS

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ABSTRACT

We present a dispersion relation formulation of the open line amplitude for the x-ray edge problem within the contact potential model. Using both multiple scattering and determinant techniques we find that to a very good approximation, the many body effects can be described within a single particle transition rate expression using a renormalized matrix element. This renormalized matrix element may be expressed exactly in terms of a frequency integral over the scattering phase shift for the core hole potential. There are small corrections to the transition rate due to multiple particle-hole pair final states and a systematic series expansion for these is presented. This series is summed at threshold to yield an exact expression for the critical amplitude multiplying the power law singularity. Our analytic results give an exact description at threshold and are shown to be quite accurate away from threshold. Comparison with the asymptotic expression of Nozieres and De Dominicis is made.

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I. INTRODUCTION

Since the original work of Mahan[1], there has been considerable interest in many body effects at x-ray absorption (and emission) thresholds in metals.[2-8] Absorption of an x-ray photon injects an extra electron into the conduction band and simultaneously turns on the core hole potential. Mahan found in a perturbation theory of this process that the cross section exhibits a power law singularity at threshold

$$I(\omega) \sim (\Lambda/\omega)^{2g} \qquad (1.1)$$

where ω is the photon energy relative to threshold, Λ is an energy of order the Fermi energy, and g is a measure of the strength of the core hole potential seen by the conduction electrons. Nozieres and De Dominicis[2] subsequently obtained a solution to the problem which is exact asymptotically close to threshold. They found

$$I(\omega) \sim (\Lambda/\omega)^{(2\delta(0)/\pi)-\alpha} \qquad (1.2)$$

where $\delta(0)$ is the core hole potential scattering phase shift at the Fermi level in the final state angular momentum channel. The parameter α is given by (ignoring spin)

$$\alpha = \sum_{\ell=0}^{\infty}(2\ell+1)(\delta_\ell(0)/\pi)^2 \qquad (1.3)$$

and arises from the Anderson orthogonality catastrophe.[9] The Mahan, Nozieres, and De Dominicis (MND) theory has been applied to experimental studies of x-ray edges[10] and has also been found relevant to the Kondo problem.[11]

One of the difficulties in the analysis of experimental x-ray spectra is that the MND theory is rigorously valid only asymptotically close to threshold. Experimental resolution and core hole lifetime broadening make this region inaccessible. There has been considerable recent theoretical progress on extending the solution away from threshold using what are essentially exact numerical solutions to the problem,[7,8,12,13] but unfortunately little progress has been made analytically. Pardee and Mahan[14] have presented a dispersion relation expression for the x-ray edge amplitude which takes into account the frequency variation of the scattering phase shift away from threshold. However, there are ambiguities in this approach since one of the required functions cannot be fully determined and the validity of the derivation itself is not self-evident.

We present here a calculation for the contact potential model in which an infinite subset of diagrams in the perturbation theory is exactly summed analytically yielding a result which is similar in form to that of Pardee and Mahan but without any of the associated ambiguities. Our central result is that we find to a very good approximation, that the many body effects in the open line amplitude (the amplitude for injecting the extra electron) can be described within a single particle transition rate expression using a renormalized matrix element. This renormalized matrix element may be expressed exactly in terms of a dispersion integral over the scattering phase shift for the core hole potential.

There are corrections to the transition rate due to multiple particle-hole pair final states and a rapidly convergent expansion for these is presented. An important feature of the present work is that this series is summed at threshold to yield an exact value for the critical amplitude multiplying the power law singularity in the open line propagator. Our analytic results which are exact at threshold are shown to be quite accurate away from threshold.

Our main results may be briefly summarized as follows. We obtain for the transition rate to zero pair final states

$$R(\omega) = 2\pi\rho(\omega)\theta(\omega)\ \exp\left\{ \mathrm{Re}\ \frac{2}{\pi}\int_0^{\Lambda} d\nu\ \frac{\delta(\nu)}{\nu-\omega}\right\}. \tag{1.4}$$

A more complicated (but explicit) expression is obtained for the transition rate to arbitrary final states. The zero pair approximation to the critical amplitude is A_0=0.866, the one pair contribution is A_1= -0.11A_0, while the total value for the critical amplitude is A = 0.788. In units where the integrated oscillator strength is one half, the zero pair term contributes S_0=0.574 and the sum of the integrated strength for the zero and one pair terms is S_0+S_1=0.475.

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AB INITIO CALCULATIONS OF DEEP CORE LEVEL SPECTRA

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We report on first-principles calculations of the one-electron inner-shell absorption cross-section for molecular systems and clusters of atoms embedded in a matrix. The theoretical framework is that provided by the many-body theory. The effective potential for the excited electron is the localized version of a Dyson self-energy non-local spectra in the framework of a local density approximation. Technically we solve the resulting Schrödinger-like equation for a non-spherical system like a molecule by using the multiple scattering $X\alpha$ method set up by Johnson and co-workers for bound states, adapted to include the many-body effective potential and the boundary conditions appropriate to a scattering state.

We emphasise that the muffin tin approximation inherent in such a method can in some cases swamp the subtleties introduced in the theory by taking into account many-body effects. Indeed, an $X\alpha$ potential yields the same results for the continuum absorption spectrum as the more sophisticated Hedin effective potential for valence excited states.

The results of the computations for some systems show how near-edge spectral features are a sensitive function of the effective potential seen by the extended electron in the molecular environment and suggest that the detailed interpretation of these features has the potential to yield useful information on the chemical oxidation state, co-ordination symmetry and molecular potential of absorbing atoms in complex environment.

Despite the limitations of the muffin-tin approximation, we show that in all cases that were studied the qualitative and semiquantitative features of the spectra are reproduced in a satisfactory way. Enhancement effects due to molecular environment, shape resonances phenomena, atomic type features are illustrated by a choice of specific examples.

DYNAMIC SCREENING BY CONDUCTION ELECTRONS AFTER A CORE HOLE EXCITATION

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After a core hole photoexcitation, the conduction electron gas relaxes around the two charges that have been created. Depending upon the velocity of the photoelectron, the Fermi gas may stay in its fundamental state (adiabatic limit) or be projected in an excited state (sudden limit). With a simple semi-classical model we describe the main physical features of the relaxation in the whole kinetic energy range and derive the consequences for the photoemission spectrum (XPS) and the absorption extended structures (EXAFS).

MANY-BODY EFFECTS AT THE 3p THRESHOLD IN METALS AND ATOMIC VAPOURS

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Resonant photoemission involving super-Coster-Kronig transitions was observed a few years ago in Ni metal by Guillot et al. [1]. For photon energy near the threshold (~ 66 eV) at which the 3p core levels are excited, it was found that the intensity of one of the structures observed by photoemission (6 eV below E_F) was greatly enhanced. It was explained as due to the autoionisation of an excited quasi-discrete atomic configuration ($3d^9 4s$). into a continuum of excitations with two holes in the 3d shell ($3d^8$). This model depended crucially on the existence of unoccupied 3d states [2]. Contrary to what was generally expected, a similar but much weaker (by one order of magnitude) two-electron resonance was observed in Cu and Zn [3] . A new mechanism was proposed by Davis and Feldkamp [4], it was based on the strong interaction between the 4s-4p conduction electrons and the two bound holes in a way similar to the X-ray edge problem.

The first part of this talk will be devoted to a review of the recent photoemission experiments which have been able to solve most of the problems concerning complicated metals such as Ni.

The second part will deal with experiments on atomic Cu [5] and the observations of the $3d^8\ 4s^2$ satellites. When the photon energy reaches the excited states below the 3p ionisation threshold, only one of the multiplets (1G) shows an appreciable resonance in agreement with theoretical calculations. Comparison with Cu solid and Cu phtalocyanine will be made.

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Abstract for the Symposium

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Phonon Effects in the Core Spectra of Alkali Halides.

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Since long ago it is known that core excitons in alkali halides have a gaussian lineshape because of the strong core-exciton phonon interaction(1). But only recently high resolution spectroscopy and modulation spectroscopy in the far ultraviolet allowed to begin a detailed study of the core-exciton phonon interaction and to find effects other than line shape broadening. In this contribution we shall discuss thoroughly the case of the Li^+ 1s-2p exciton in LiF(2).

The shift with temperature of core levels in alkali halides rests almost entirely on the variation of the Madelung energy, as shown by the x ray photoemission spectra of LiF measured at several temperatures. Thus, the threshold for transitions starting from the alkali levels increases with temperature, while the opposite occurs in the case of initial halide levels. Thermomodulation experiments performed at the fundamental threshold and at the Li^+ 1s threshold in LiF (as well as at the Rb^+ 4p and K^+ 3p thresholds in the corresponding halides) indeed show such a behavior. While the fundamental exciton series follows rigidly the fundamental gap to higher energies upon cooling, the Li^+ 1s-2p exciton does not follow the Li^+ 1s threshold to lower energies. On the other hand, if we consider the Li^+ 1s-2p exciton as a localized transition, it should not shift with temperature. Thus, its experimental negative temperature coefficient must arise from exciton phonon interaction.

From available theories for exciton phonon interaction (based on the linear coupling approximation) we obtain that the coupling constant for the Li^+ 1s-2p exciton falls in the intermediate coupling range. A 1.1 eV self energy for the exciton in the phonon field is derived. Several consequences, in agreement with experiment, can be deduced and are discussed. However, an unrealistic core-exciton band width of 1.4 eV is obtained.

By describing the core-exciton following a localized picture (as an F center), in order to have a negligible exciton band width, we find again agreement with several experimental observations. But, in this case, strong exciton phonon coupling is necessary and the temperature shift of the exciton peak is due to non-linear terms in the exciton phonon interaction.

Further experimental as well as theoretical efforts for investigating the core-exciton phonon interaction in more detail are outlined.

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PHOTOELECTRON AND AUGER ELECTRON SPECTROSCOPY OF CORE STATES IN ATOMS

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Excitation or ionization of a core-level (inner-shell) electron can lead to a subsequent autoionizing or Auger decay, respectively. In this contribution I will concentrate on processes where the excitation or ionization of the inner-shell electron is caused by photon impact because this is a very clear case for the demonstration of fundamental phenomena which show up in the spectrum of ejected electrons. As a starting point, one can classify different groups in the spectrum of ejected electrons caused by photon impact: a) Resonance excitation of an inner-shell electron can be followed by the emission of autoionizing electrons (their kinetic energies are fixed by that of the resonance state and that of the final ionic states). b) Ionization of an inner-shell electron gives photoelectrons (their kinetic energy follows the photon energy) and Auger electrons (their kinetic energy again is fixed by the ionic states involved in the transition). However, it should be kept in mind, that photoelectrons and Auger electrons originate from the same primary photoionization event and that autoionizing decay of an inner-shell resonance-excitation can interfere with an outer-shell ionization process. Therefore, the distinction of the ejected electrons into different groups may fail completely.

It is the aim of this contribution to demonstrate the relations between the different kinds of ejected electrons on selected examples. Guidance shall be given by a classification of the processes with regard to the photon energy as compared to the binding energy of the inner-shell electron:

1) ionization with photons of high energy (sudden approximation)
2) ionization with photon energies close to the threshold (post-collision interaction)
3) excitation by photons (and decay of the resonance).

Before going into the detailed discussion, two remarks shall be made: i) The main aspects of the phenomena to be described have found already great interest in the literature (see for example Ref. 1 - 7). Here a simple discussion from an experimental viewpoint shall be made. ii) The phenomena to be discussed will occur also in particle-impact processes but there they are more complex: The generally broad range of energy transfer in the collision process allows not only ionization but also excitation processes at the same time (see for example Fig. 2 of Ref. 8). In addition, in particle-impact processes, especially in heavy-particle impact one has to consider also higher orders of the Born approximation and one has to take into account also the electrons of the incoming particle (molecular orbital model); as example see the comparison of neon-Auger spectra produced by different particles as given in Fig. 10 of Ref. 9 and Fig. 8 of Ref. 10.

1. Ionization with photons of high energy

Photoelectrons and Auger electrons originate from the same primary ionization event. Therefore, the correct theoretical treatment should handle them in a unified manner. This is a general statement which is valid independent of the photon energy. Especially at high photon energy, a separation of the photoelectron spectrum from the Auger spectrum is possible in many cases. A necessary prerequisite for such a separation is that the energies of the final ionic states after the photoionization and of the Auger transition differ considerably. Otherwise, if the energies are of the same order, an unified treatment might be required. One

example shall be given for each case.

a) Unified treatment of photoelectrons and Auger electrons

Photoionization of the 4p-electron in xenon is an illustrative example for the case where the emission of photoelectrons and Auger electrons cannot be handled as independent processes. Here the single-particle energy of the ion after the ionization process is very close to the single-particle energy of the final Auger electron configuration of two missing 4d-electrons (compare Fig. 1, upper part). This makes it understandable that configuration interaction (CI) exists between $4p^5\,4d^{10}\,5s^2\,5p^6$ and $4p^6\,4d^8\,5s^2\,5p^6\,kf$. k stands for discrete excited states (n) as well as for the continuum (ε). It is obvious that this CI will be extremely strong when electrons of the same principal number n are involved because then all wave functions overlap very strongly in the CI nondiagonal matrix element. This happens in the xenon example for $n = 4$. As a consequence of this extreme strong CI, the single-particle levels of $4p_{1/2}$- and $4p_{3/2}$-ionization are distributed over a broad energy range, and the sharp peak comes from a strongly localized $4d^8\,5s^2\,5p^6\,4f$ excitation. This is demonstrated in the spectral weight function of the 4p-core hole (see Fig. 1, upper part); for more details see Ref. 2. In this example the energies are such that the process which goes to the continuum also allows real Auger transitions ($E_{kin,Auger} > 0$) and not only virtual processes (which describe CI). This establishes the strong coupling between the emission of photoelectrons and Auger electrons described here in the CI model.

The spectral weight function of the core-hole determines the spectrum of the photoelectrons (simply via the energy relation $E_{kin,phe} = h\nu - E_B$). The Auger spectrum is determined by the condition $E_{kin,Auger} > 0$ and the convolution of the spectral weight function of the inner-shell hole with that of the two final holes (Ref. 1).

b) Separated treatment of photoelectrons and Auger electrons

Photoionization of the 1s-electron in neon (compare Fig. 1, lower part) is an illustrative example for the other case where the emission of photoelectrons and Auger electrons can be separated. Here the spectral weight function of the inner-shell hole is determined by the photoionization process of the 1s-electron whereby relaxation and CI effects have to be taken into account*) but no real Auger processes. With the help of Fig. 2 it shall be demonstrated for the example of neon how the spectra of photoelectrons and Auger electrons are related to each other. The total photoelectron spectrum (Ref. 12) shows the strong 1s-photoline (normal line) and several much smaller lines together with a smooth continuum (satellites). The most intense discrete satellites come from electron configurations $1s\,2s^2\,2p^5\,np$, and the continuum from $1s\,2s^2\,2p^5$. Let us follow first the Auger decays from the intense normal line (sketches of the relevant electron configurations are on the right side of Fig. 2). When the 1s-hole is filled-up by the Auger transition, electrons from the 2s and/or 2p shells are involved; their possible states give in LS-coupling the five normal Auger lines (the transition to $2p^4\ {}^3P$ is forbidden in LS-coupling by selection rules). But, double Auger transitions can occur also. These double Auger transitions involve three electrons and are caused by electron correlation effects. It should be noted that especially the double Auger processes to the continuum are quite intense (7,5% with respect to all Auger transitions; for more details see Ref. 13, 14). Next let us follow the Auger decays connected with the satellites in the photoelectron spectrum (sketches of the relevant electron configurations are on the left side of Fig. 2). The decay of discrete photo-satellite states follows two paths: the excited electron stays in its orbital when the inner-shell hole is filled (spectator transition) or it participates in the transition (participator transition). The most intense contribution (12,4% with respect to all Auger transitions in the spectrum of Ref. 8) besides the normal

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*) Relaxation and CI have the same origin, namely electron correlation effects; for more information see Ref. 11.

Auger spectrum comes from the satellite continuum in the photoelectron spectrum. As a result of all these individual processes, the total Auger spectrum in the lowest part of Fig. 2 is achieved (Ref. 8, *)). It can be seen that even for such a simple case as 1s-photoionization in neon the resulting Auger spectrum is very complicated, here about 90 lines have been analyzed (Ref. 8). Coincidence experiments between a selected energy region of photoelectrons (normal line or satellite line or even part of the satellite continuum) and the resulting subsequent Auger lines or vice versa would be a powerful tool for the interpretation of more complex spectra (Ref. 16).

2. Ionization with photon energies close to the threshold

When the photon energy is close to the threshold for the ejection of an inner-shell electron, the subsequent Auger decay may be influenced by the presence of the slow ejected photoelectron. This is a manifestation of the so-called post-collision interaction (PCI). Therefore, PCI requires again a unified treatment of photoelectrons and Auger electrons. But, for cases where at high photon energy a separated treatment of photoelectrons and Auger electrons is possible, the PCI phenomena can be described much simpler in two equivalent ways: (i) as a relaxation process i.e. the slow photoelectron suddenly moves in a changed potential when the fast Auger electron is ejected or (ii) as a shielding effect i.e. the slow photoelectron partially screens the ionic field and therefore the ejected faster Auger electron sees a smaller attractive potential (compare Fig. 3, upper part). As a consequence of this PCI, the Auger electron gains the energy ϵ and the photoelectron looses the same amount. Experimentally, this can be seen as a shift and broadening of the corresponding lines in the electron spectrum. This is illustrated

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*) A comparison of this Auger spectrum for photon and electron impact, respectively, is given in Ref. 15.

clearly in Fig. 3, lower part, on the xenon $N_5 - O_{23}O_{23}\ {}^1S_0$ Auger peak (at 29.93 eV kinetic energy in the limit of high-energy photons). At the "high" photon energy of 110 eV (i.e. 42.45 eV above the threshold for $4d_{5/2}$ - ionization) it has a symmetrical shape (convolution of a Lorentzian shape and of the spectrometer function) and it is positioned close at the energy of 29.93 eV (at this photon energy the estimated PCI effect is equal to the experimental uncertainty in the determination of energy shifts which is ± 30 meV). At 67.75 eV photon energy (0.2 eV above the $4d_{5/2}$ - ionization threshold) this Auger peak has shifted towards higher kinetic energies which results in a shift of the maximum by 264 meV and an asymmetrical shape. For simplicity, the PCI effect has been discussed here only for the energy shift and broadening of the $N_5 - O_{23}O_{23}\ {}^1S_0$ Auger peak. However, it is possible to calculate also the PCI intensity distribution of an Auger line (Ref. 17). When this PCI intensity distribution of all $N_5 - O_{23}O_{23}$ Auger peaks is taken into account together with other contributions to the electron spectrum in this energy region then the solid line in Fig. 3, lower part, is achieved which describes quite well the whole experimental electron spectrum (points in the figure). The other contributions are due to a small amount of the undisturbed $N_{45}-O_{23}O_{23}$ Auger spectrum caused by stray light and higher - order diffraction in the monochromator, the contribution of the 5s - photoionization spectrum (5s - photopeak at 44.4 eV kinetic energy) with its satellites and a straight - line background. For more details see Ref. 18, for the influence of PCI on the photolines in Xenon compare Ref. 19.

3. Excitation by photons and resonance decay

The discussion in paragraphs 1 and 2 has given examples for separated and unified treatment of photoelectrons and Auger electrons, but still it was possible to distinguish between both groups of electrons because of their different kinetic energies. This situation changes when the

photon energy fits to the excitation of an inner-shell electron (resonance excitation). Here the autoionizing decay of this resonance procuces final ionic states which are the same as from photoionization processes with a more outer-shell electron. Therefore, interference effects can occur which then destroy the distinction between photoelectrons and electrons from the autoionizing decay. The interference of different decay channels of the resonance with direct photoionization processes in a more outer-shell is equivalent to the treatment of CI between a discrete state with several continua of different electron configurations. This CI is responsible for the characteristic Fano - Beutler line-shape with the profile indices E_r, Γ, q and ρ (for photoabsorption see Ref. 20, 21; for electron emission see Ref. 22).

In order to illustrate the foregoing considerations, the electron spectrum which includes the decay of the photoexcited xenon resonance $4d^9\ ({}^2D_{5/2})\, 5s^2\, 5p^6\, 6p\ {}^1P_1$ shall be discussed in more detail (compare Fig. 4). This resonance with $E_r = 65.11$ eV and $\Gamma = 0.11$ eV is very specific because the Fano - Beutler profile indices q and ρ in the absorption spectrum (Ref. 23) are such that the cross section is well described by a Lorentzian line shape (q = approx. 200) and the interaction with the continua is small (ρ^2 = approx. $3 \cdot 10^{-4}$). Even though this knowledge of the profile indices q and ρ in the absorption spectrum does not provide sufficient information about the profile indices of each individual decay channel in the electron emission spectrum (Ref. 24), as a first approximation, we will assume for this example small CI between the resonance and their continua of the individual decay channels. Then we can separate incoherently the resonance decay spectrum from the ionization spectrum, the sum of both gives the experimentally observed spectrum. Both components are shown in Fig. 4. First, it can be seen clearly that the direct photoelectron spectrum off resonance changes completely its structure when resonance excitation occurs. This change would be even more dramatic for a photon band-pass BP comparable to the resonance width Γ (in this experiment it was BP about 6 times larger than Γ). The other interesting feature in this resonance spectrum are the different decay channels (compare also Ref. 25, 26). As in the discussion of the neon Auger spectrum, we can classify them accordingly to participator and spectator transitions, and also three-electron transitions (equivalent to the double Auger transitions in the neon case) can be found in the spectrum. It is hoped that the detailed analysis of such resonance - decay spectra can elucidate the composition of the resonance state (Ref. 25, 27, 28).

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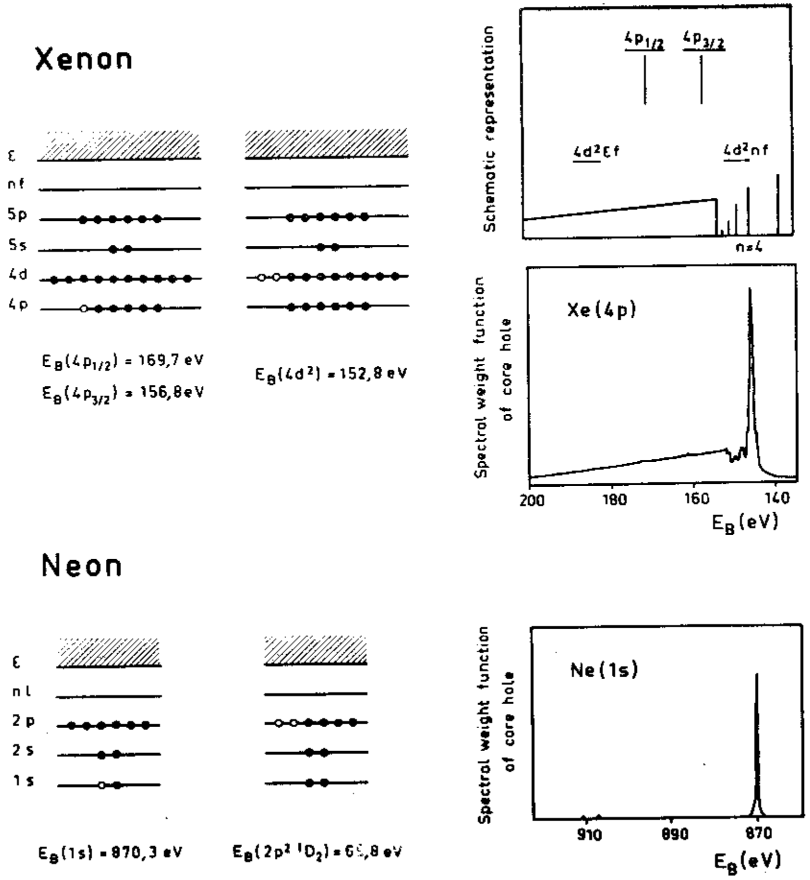


Fig. 1. Compilation for 4p - photoionization in xenon and 1s - photoionization in neon.

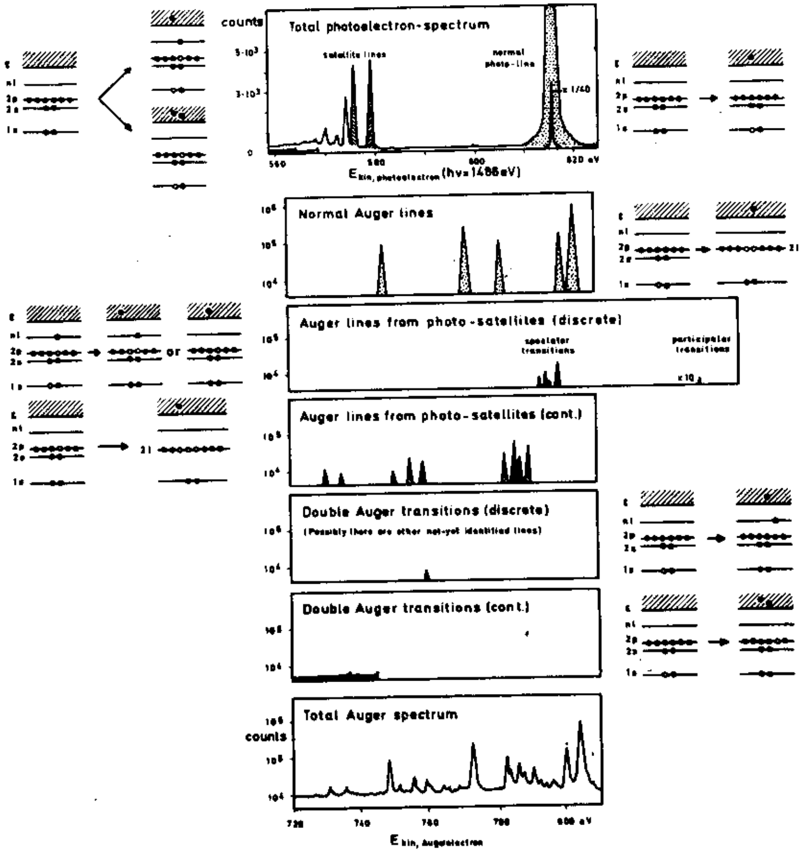
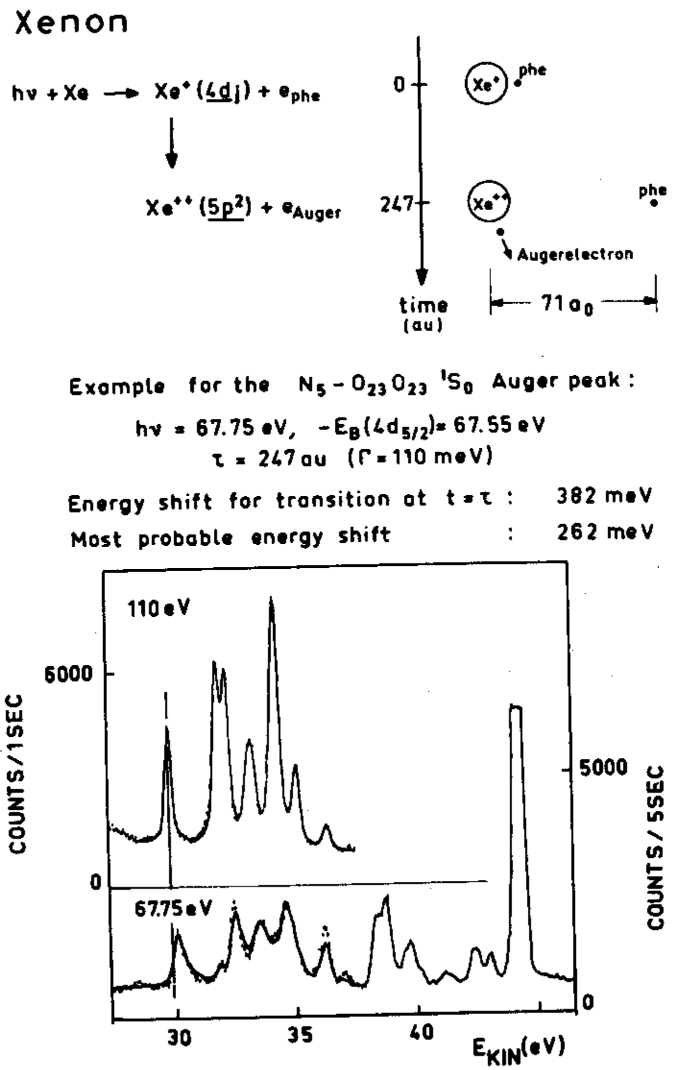


Fig. 2. Compilation for 1s - photoionization and subsequent Auger decay in neon (spectra from Ref. 12 and Ref. 8).



Example for the $N_5-O_{23}O_{23}$ $^1S_0$ Auger peak:

$h\nu = 67.75$ eV, $-E_B(4d_{5/2}) = 67.55$ eV

$\tau = 247$ au ($\Gamma = 110$ meV)

Energy shift for transition at $t = \tau$: 382 meV

Most probable energy shift : 262 meV

Fig. 3. Compilation for PCI in the xenon N_5-$O_{23}O_{23}$ Auger spectrum (spectra from Ref. 18); the symbol $\underline{n\ell}$ means that an nℓ electron has been ejected.

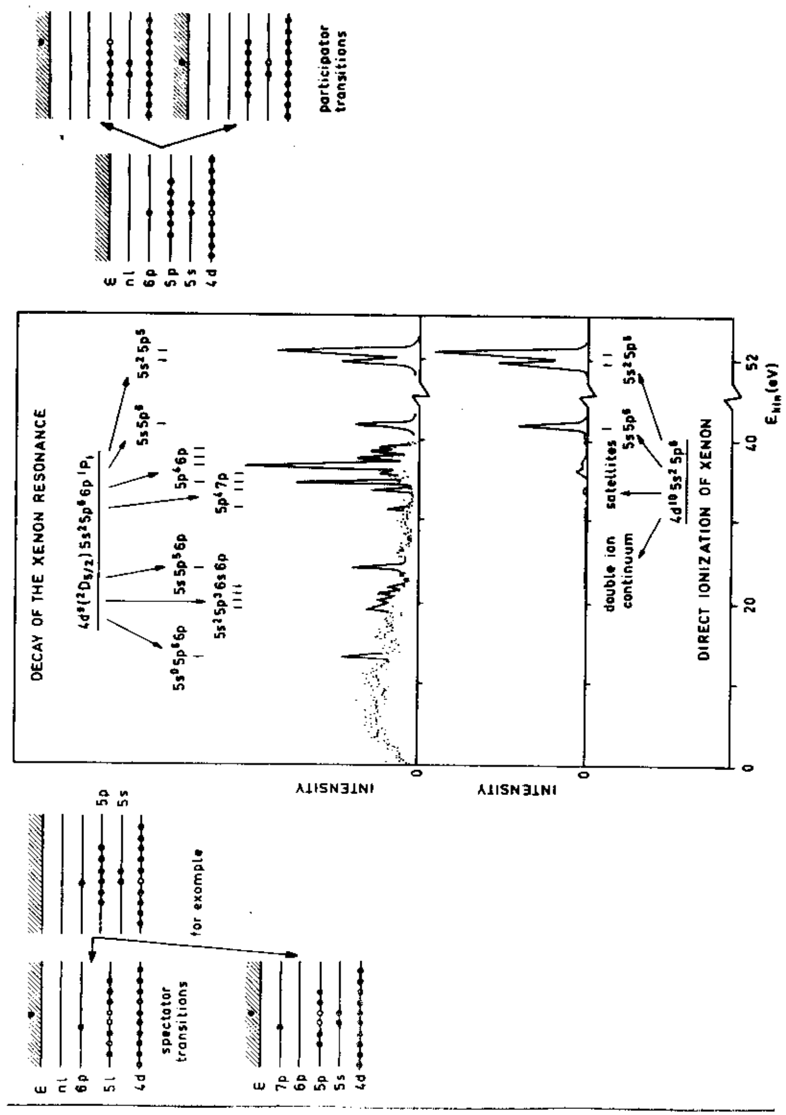


Fig. 4. Compilation for the $4d^9(^2D_{5/2})\,5s^2\,5p^6\,6p\,^1P_1$ xenon resonance - decay (spectra from Ref. 29).

Temperature Dependence of Shallow Core Excitons

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At the onset of electronic excitation from core levels in insulators and semiconductors usually sharp and often well-resolved spectra are observed which are associated with excitons. They are caused by electron-hole interaction, which dominates the core spectrum at threshold. The excitonic spectra look complicated in many cases but carry much information concerning the elctronic and geometrical structure of solids and interactions, e.g. exciton-phonon interaction.

The interesting features to be studied are

(1) the electronic excitation spectrum including position and oscillator strength of the transitions measured at temperatures as low as possible to reveal all fine structure, binding energies of excitons etc;

(2) line shifts, halfwidths, line profiles as a function of temperature to obtain information on exciton-phonon interaction;

(3) surface effects.

Here we shall only briefly summarize the main results on the electronic interpretation of selected core excitation spectra and then rather concentrate on the elctron-lattice interaction, which has been studied through the temperature dependence of the electronic spectra.

The aim of our investigation was to study shallow core excitons in representative insulators and semiconductors in the 10-30 eV range with high resolution, at least one order of magnitude better than the smallest observed line width. An effective method is to measure the reflectivity from clean ultrahigh vacuum cleaved surfaces of single crystals. The experiments were performed for the K^+3p level in potassium halides, and the Ga-3d and In-4d levels in III-V-semiconductors on oriented single crystal surfaces down to 20 K. High resolution (~ 1 meV) was provided by the 3-m-monochromator for synchrotron radiation at the DORIS electron storage ring in Hamburg.

The K^+3p excitons in K halides show an excitation spectrum ($3p \longrightarrow 4s,3d$) consisting of a number of sharp lines due to strong localized electron-hole interaction. They also reveal strong exciton-phonon-coupling. This is observed best in the temperature dependence of the linewidth. The magnitude of the linewidth is strongly anion dependent as expected from LO-phonon-coupling. The spectra show a remarkable similarity to the absorption of color-(F)-centers as regards the magnitude and temperature behaviour of the linewidth and the temperature shifts of the peak.

On the other hand the observed temperature coefficients of the shallow core excitons of III-V compounds in which electron-hole interaction is weak appear to be describable by weak electron-phonon coupling. Both initial and final state contributions have to be considered. The volume electronic transitions and their temperature dependence can be related to the properties of the critical points L,X in the lowest conduction band. Phonon and hydrostatic contributions are important for explaining the temperature dependence.

Reflection spectroscopy in this energy range proved to be surface sensitive as shown for semiconductors by the observation of surface excitons on clean cleaved crystals and by the disappearance and shifts of structure with exposure to gases and for rough surfaces.- Further theoretical work seems desirable to improve the quantitative understanding of several aspects of the electronic, vibrational and surface properties of shallow core excitons.

For detailed references see:

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DYNAMICAL CONCEPTS IN X-RAY PHOTOEMISSION

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The purpose of this talk is to provide the background for the understanding of some recent experiments in core level spectroscopy, in particular the many-body effects in X-ray photoemission from core levels near metallic surfaces (including adsorbates).

First, a general discussion of various dynamic phenomena in XPS is given, e.g. the concepts of sudden vs. adiabatic approximation, transient effects, intrinsic and extrinsic excitations, interference effects, spectral sum rule and its possible breakdown, potential switching effects, etc., with a special emphasis on the differences between the situation in atomic and solid state photoemission.

Next, the theoretical description of the photoemission spectrum is discussed, and the new formulation is presented, which provides a scheme for perturbative as well as nonperturbative treatments of various scattering mechanisms in XPS.

Finally, this theoretical approach is applied to the discussion of inelastic effects in XPS from core levels near metallic surfaces, in particular the interaction of the electron--hole pair with the bulk and surface plasmons, phonons and soft electronic excitations, and the qualitative consequences of these dynamical phenomena on the overall shape of the photoelectron spectra.

Phonon Effects on Core Level Excitations

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The following topics of phonon effects on the core or valence state excitation and deexcitation processes in insulators will be discussed.

1. Temperature dependent widths and shifts in the core absorption spectra.

2. Possibility of Jahn-Teller splitting in the absorption spectra from the orbitally degenerate core states.

3. Various possibilities of lattice relaxation around the optically produced core (or valence) hole and exciton, such as one- and two-center types with or without bubbles, depending on the core orbital state and on the on-site and intersite electron-phonon interactions.

4. The effect of lattice distortion around the core hole upon the valence electron states, which may cause satellites to the continuous emission spectra of the valence band, corresponding to the bound states of valence hole in the final state.

5. Incomplete lattice relaxation around the optically produced core hole or exciton due to the limited lifetime of the latter, and its manifestation in the optical spectra.

Many-body effects in core spectra of transition metals

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Many-body effects exist in such a variety and influence spectra in so many ways that an overview becomes meaningless in a short talk like this. I shall therefore limit myself to treating a specific group of experiments and spectroscopies, and within that framework a limited number of many-body effects. The physical process to be considered is electron impact excitation and emission of electrons and X-rays, which encompasses electron energy loss spectroscopy (EELS), Auger electron spectroscopy (AES), X-ray emission spectroscopy (XES), bremsstrahlung isochromat spectroscopy (BIS) and appearence potential spectroscopy (APS). Fig. 1 shows the fundamental excitation and emission processes

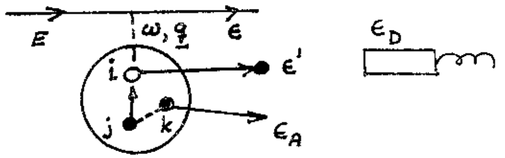

Fig. 1

In the EELS mode the detector energy ε_D is swept while E is kept constant. In isochromat type of modes, the detector is set at a constant energy ε_D and the incident energy E is swept. In addition to an EELS-like spectrum, this gives excitation functions for Auger lines, autoionization lines etc.

The role of many-body effects depends strongly on the values of the incident energy E, the energy and momentum transfers ω and q, and the Auger energy ε_A, since these determine which core level is primarily excited, what are the kinetic energies of the final state electrons, in which levels or bands are the final state holes etc. Generally speaking, many-electron effects are important when holes and electrons in the intermediate and final states have strongly overlapping wave functions, leading to large interaction strengths, strong polarization effects and rapid decays[1-4]. Particularly strong and spectacular effects often occur near thresholds for core electron excitation or ionization, in which case the final state electrons ε and ε' are left in the vicinity of the Fermi level, e.g. in the empty part of the high-level-density d-band, and may correlate strongly with the holes and electrons in the excitation region[5-7]. As a consequence there may be strong polarization effects, the final state electrons may take part in the decay, and there may be no clear separation between excitation and emission processes. This will lead to distortions and shifts of Auger lines (post-collision interaction (PCI) effects)[6,7], and to resonances in electron energy loss features and in Auger and autoionizing lines.

In this talk I shall discuss in some detail the following points:

1) Electron energy loss and photoionization spectra of the 3d-metals in the vicinity of the 3p-threshold, in terms of screening and collective effects. I shall also discuss atomic versus solid state effects and present some results of calculations in the random phase approximation based on Hartree-Fock and local-density wave functions.

2) 3p (4p) hole spectra in the 3d (4d) transition metals in terms of super Coster-Kronig and giant Coster-Kronig fluctuation and decay processes[4]. This also includes Auger spectra where one or both of the final state holes belong to 3p (4p), e.g. the M_{45}-$N_{23}N_{45}$ Auger spectrum in Pd[8]. We also note that 3s (4s) holes are influenced in a similar way.

3) Resonances in electron and X-ray emission spectra when the incident energy E lies in the vicinity of the 2p-thresholds in the 3d-transition metals. This includes distortions and shifts of Auger lines due to PCI[9], resonances in Auger and X-ray[10] lines, resonances in electron energy loss features and bremsstrahlung[5,10] peaks. We shall also compare with the corresponding processes in Ba, La and Ce, involving localized 4f-levels[11].

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SPECTROSCOPY OF CORE LEVELS OF LANTHANIDE AND ACTINIDE COMPOUNDS

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The radiative channel of the decay of quasi-localized continuum states accounting for "giant" resonances in ultrasoft X-ray absorption spectra of rare earths (RE) and their compounds above the 4d threshold will be discussed [1-4].

In the 4d emission spectrum of La in La_2O_3 obtained at the accelerating voltage of 500 V, a strong and wide emission band is observed which cannot be described as a transition between one-electron X-ray levels and whose energy position coincides with that of the giant resonance in the 4d absorption spectrum [4]. In our earlier studies of RE emission spectra at high accelerating voltage (minimum electron energy being 1.5 KeV) the effect of self-absorption has essentially distorted the spectrum above the 4d threshold, and therefore we did not observe high-intensity radiation in the region of the giant resonances [1-3].

The studies of the La 4d emission spectra in different compounds have proved the atomic nature of the radiation in the region of the giant resonance. The emission intensity in the region of the resonance appears to be comparable to the intensity of the inner $4d \rightarrow 5p$ line. The band width of the emission spectrum has been found to be essentially broader than that of the absorption spectrum.

A calculation [5] of the La emission spectrum for transition between the levels of the $4d^9\,4f$ (^3P, ^3D, ^1P) and $4d^{10}$ ($^1S_0$) configurations will be discussed. In the calculation both radiative and Auger level widths of the excited configuration have been taken into account. Results show that the intensity of the radiative transitions from the broad autoionizing $4d^9\,4f\ ^1P$ level, that can be connected with the giant resonance, is many orders higher than that from the other two levels lying below the 4d threshold and generating two weak narrow emission and absorption lines at the low-energy side of the resonance. The results of the calculation, although carried out in the frame of a rough model, do not contradict experimental data.

Another theoretical approach to the interpretation of emission bands above the threshold [6] is to calculate the bremsstrahlung radiation resulting from inelastic scattering of fast electrons on atoms. A "polarizational" part of the bremsstrahlung radiation depends on the oscillator strength of the atomic transition to the continuum, and if the giant resonances above the 4d threshold in RE absorption spectra are observed, they can also be expected to appear in the bremsstrahlung spectrum, this assumption is supported by La spectrum calculations. As to the energy position and form, the band in the calculated bremsstrahlung spectrum practically coincides with that of the La 4d absorption spectrum.

The difference between the models used for the calculation of the bremsstrahlung radiation in the regions of the 3d threshold [7] and the 4d threshold [6] will be discussed.

The report will touch upon results of the investigation of the Ce 4d emission spectrum in Ce O_2 at 500 V in which a strong emission band in the region of the giant resonance has been observed as well. The conclusion has been drawn that the radiative decay of excited states accounting for the giant resonances is characteristic of all rare earths in whose absorption spectra such resonances appear.

We shall analyse absorption and emission spectra of Th in ThO_2 and U in $U_3\,O_8$ in the region of the 5d thresholds [8]. These spectra also reveal strong absorption and emission bands above the 5d thresholds. The bands nearly coincide in the energy (the emission band is somewhat shifted towards lower energies).

There are both a similarity and a difference in the structure of the 4d spectra of La and 5d spectra of Th. If we try to give these spectra a similar interpretation, then the $5d^9 5f\,^3D$ level of Th should be ascribed a greater oscillator strength than the $4d^9 4f\,^3D$ level of La.

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