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Experimental study of the $3p$-$3d$ intershell interaction in Ca, Sc, Ti, V, and Cr metals

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The photoionization cross section of the $3d$ valence band is obtained for Ca through Cr in the photon-energy range between 15 and 150 eV. Strong interference-like resonances are observed in the region of the $3p$ threshold. The resonances show a double structure probably due to shakeup effects.

The interest in resonance photoemission from transition metals has experienced a strong revival due to firstly, the observation of spin polarization of resonantly emitted electrons.[1,2] and secondly, the sensitivity of photon-stimulated desorption from solid surfaces to decay mechanisms of resonantly excited core states.[3] This has stimulated several recent experiments such as the investigation of two-electron versus one-electron resonances in Cr, Fe, and Co by Chandesris *et al.*,[4] the observation of resonant electron emission in Ti and TiO_2 by Bertel *et al.*,[5] and an investigation of resonance recombination lines in electron-excited Auger spectra of all $3d$ transition metals by Zajek *et al.*[6]

In the present paper we report a systematic study of the $3p$-$3d$ interaction in Ca and the light $3d$ metals Sc through Cr. As an extension of the earlier work on Cr (Ref. 7), the present study takes advantage of recent progress in extracting partial subshell cross sections from raw photoemission intensities measured on solids.[8] Our data provide strong evidence that shake-up excitation plays an important role for the $3p \rightarrow 3d$ resonance. It is in this respect that the results may also contribute to a more general understanding of the $3p$-excitation spectrum since x-ray photoelectron spectroscopy (XPS) of the $3p$ electrons also reveals strong contributions of satellites which are not yet explained.

The outline of the paper is the following. In the first section we give a brief description of the experimental setup. The results for the $3d$ intensity versus photon energy of Ca and the $3d$ metals Sc through Cr are presented along with details of the data-evaluation procedure. The second section contains the discussion of the results which are compared in particular with atomic data and XPS spectra. A model is proposed which explains the energy distribution curves (EDC's) taken at photon energies within the $3p \rightarrow 3d$ resonance to originate from shake-up excitations which do not decay into single-hole final states. In the third section we compare the present results to other recently published data of the $3p$-$3d$ interaction in the light $3d$ metals.

I. EXPERIMENT, DATA EVALUATION, AND RESULTING $3d$ CROSS SECTIONS

The experiment was carried out at the Hamburger Synchrotronstrahlungslabor HASYLAB, West Germany. Synchrotron radiation from the storage ring DORIS was monochromatized by the FLIPPER monochromator.[9] The use of a tunable light source permitted the exploitation of special photoemission techniques (for details, see Ref. 10). Yield spectra which are compatible to the absorption were taken by constant final-state (CFS) spectroscopy, the final energy of $E_{\text{kin}}=5$ eV being set to monitor the low-energy background of inelastically scattered electrons. The valence-band intensity as a function of photon energy was measured in constant initial state (CIS) spectroscopy, the initial energy being chosen close to the Fermi level. A commercial double-pass cylindrical mirror analyzer (CMA) served to analyze the photoelectrons. The samples were evaporated from tungsten baskets onto stainless-steel substrates at a base pressure of the system of 1×10^{-10} Torr. The cleanliness of the samples was checked by photoemission and Auger spectroscopy. As main impurities, we detected iodine for the Ca sample and chlorine for Sc and Ti. The signal from the impurities corresponded roughly to a percent of a monolayer. For V and Cr, impurities stayed below the percent level.

It turned out that the most sensitive tool to check the quality of the samples is yield spectroscopy in the region of the $3p$ absorption resonance. After successive evaporations of sample material onto the substrate we monitored the decrease in intensity of contaminant-derived structures in EDC's. In addition, yield spectra and CIS spectra of the d band were taken in the region of the $3p$-resonance absorption. When EDC's did not show any changes from one evaporation to another, we could still observe intensity increases in yield spectra at the maximum of the $3p$ resonance. For V and Cr we were able to reproduce the published absorption spectrum, in particular the intensity gain between the minimum at the $3p$ threshold and the subsequent maximum. This could not be achieved for Ti; for Ca and Sc there are no reliable absorption data for such a comparison. The least sensitivity to the sample quality was found in the CIS spectra of the $3d$ band. Thus we believe that even for the cases for which ultimate sample purity could not be reached, our CIS spectra still provide reliable results.

To obtain the $3d$ photoionization cross section from measured CIS spectra, the photoemission intensity has to be normalized to the flux of incoming photons and the transmission of the electron analyzer. At the FLIPPER monochromator the photon flux is obtained by a photodiode which can be moved into the beam behind the exit slit.[8,9] The determination of the transmission of a CMA is a problem to which different approaches have been proposed.[11,12] We use a method which is described in detail by Barth *et al.*[8] to determine the variation of the CMA transmission as a function of the ratio between kinetic and pass energy of the photoelectrons. Here let us just mention that we measure the transmission by monitoring the intensity variation at fixed kinetic energy while tuning the pass energy. Because photon energy and kinetic energy are fixed the intensity variation is now only a function of the analyzer transmission. Dividing this measured intensity by the pass energy accounts for the variation due to the change in the CMA resolution. The corrected intensity plotted versus the ratio between kinetic and pass energy gives the CMA transmission.

The influence of the intensity normalization to the CMA transmission is illustrated for the $3d$ intensity of Ti in Fig. 1. The CMA transmission decreases with increasing kinetic energy of the photoelectrons if the pass energy is fixed.[8] Note that the normalization procedure essentially conserves all structures which are already present in the uncorrected curve, while noticeably affecting the overall shape of the spectrum. Basically, these normalization procedures enable us to obtain partial subshell cross sections of solids over an extended energy range which is limited only by the performance of the monochromator. But let us note in passing that absolute photoelectric yield data for cathode materials of the photodiode have only been obtained up to 180 eV photon energy.[13] Furthermore, the above corrections are only sufficient if the overall experimental resolution is small compared to the energetic width of the measured structure. As an illustration observe the inset of Fig. 1 which shows another feature of the Ti $3d$ cross section in the energy range of the $L_{\mathrm{II,III}}$ absorption edges (compare Ref. 14). To relate the intensity scale of this measurement to the data in the energy range between 15 and 150 eV, the normalization to the photon flux is based on extrapolations of the photoelectric yield of the photocathode,[9,13] and the normalization to the CMA transmission is accomplished by a correction for the intensity deterioration due to the low-energy resolution. Accordingly, a rather large uncertainty has to be adopted if cross-section measurements are compared over such an extreme energy range.

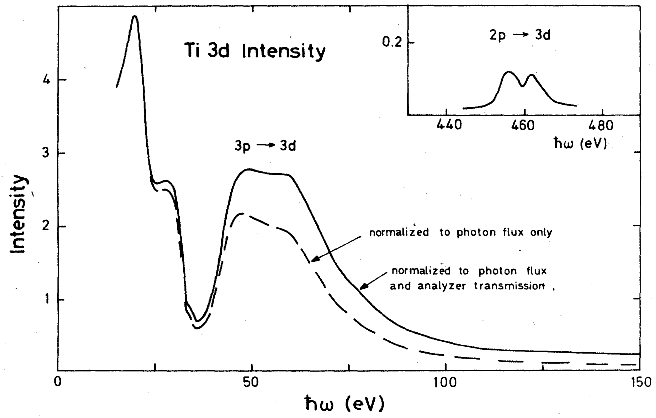

FIG. 1. Ti $3d$ cross section measured at the top of the valence band. The two curves illustrate the influence of the analyzer transmission correction. The resonance around 50 eV is due to the coupling to $3p \rightarrow 3d$ excitations; the inset shows another resonance at 450 eV due to $2p \rightarrow 3d$ excitations.

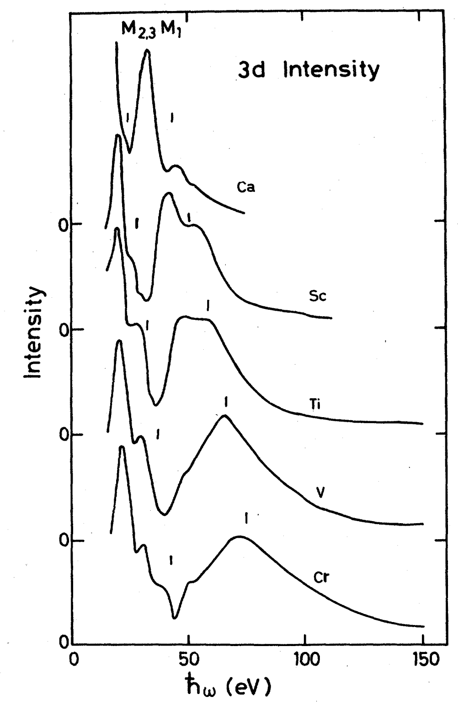

FIG. 2. $3d$ cross section for Ca through Cr, measured at the top of the valence band by CIS spectroscopy ($E_i = 0.5$ eV below E_F). The thresholds of the $M_{2,3}$ and M_1 excitations are marked by vertical bars.

In Fig. 2 we present our results for the $3d$ cross sections of Ca, Sc, Ti, V, and Cr obtained by means of CIS spectroscopy with initial energies chosen close to the Fermi level. The reason for including Ca in this series of light $3d$ transition metals is the considerable $3d$ character of the valence band at the Fermi level.[15,16] The spectra show pronounced minima at the $3p$ thresholds with subsequent maxima. Both minima and maxima exhibit a double structure (exception: just one minimum for Ca and Cr), the two maxima are separated by 10—20 eV. The energy positions of these structures are given in Table I. In the low-energy region structures appear almost independent of the element with a prominent maximum at ~20 eV and some oscillations up to the $3p$ threshold.

II. DISCUSSION OF THE 3p-3d INTERSHELL INTERACTION

In Fig. 3 the $3d$ cross sections are compared with the total absorption for Ti, V, and Cr. For this comparison we chose the optical absorption calculated from energy-loss data by Wehenkel and Gauthé[17] rather than the direct optical measurement by Sonntag *et al.*[18] which does not

TABLE I. Energy position of structures in the $3d$ cross section, XPS binding energies for the $3p$ level, and maximum positions of the $3p \rightarrow 3d$ absorption resonance. All energies are in eV.

	$3d$ cross section, this work				$3p$-XPS	$3p$-$3d$ absorption	
	Minimum 1	Minimum 2	Maximum 1	Maximum 2	Binding energies	maximum	
Ca	25		33	45	25.1/26.5[a]		
Sc	29.5	31.7	42	53	28.3[a]		
Ti	33.2	35.5	48	59	32.6[a]	45[b]	45.9[c]
V	36.6	39.5	45.5	65	37.2[a]	49[b]	47.7[c]
Cr	43.5		50	72	43.1[a]	49/54[b]	49.4/54[c]

[a] M. Cardona and L. Ley, *Photoemission in Solids* (Springer, Berlin, 1978).
[b] Reference 17.
[c] Reference 18.

cover the energy range below 40 eV. Note that both results for the optical absorption show rather substantial discrepancies for Ti and V (see Fig. 4 for V) which limit the conclusions that can be drawn from a comparison with the $3d$ cross section. For Sc, Brousseau-Lahaye *et al.*[19] have computed the absorption spectrum from energy-loss data, but the overall shape of this absorption spectrum disagrees with the results for the other members of the $3d$ series so that it is not included in Fig. 3. For Ca, optical constants have also been calculated from energy-loss data, however, no result for the absorption was given.[20]

In contrast to an atomic experiment, partial subshell cross sections of solids cannot exclusively be interpreted in terms of excitation probabilities. The probability for an excited electron to leave the solid without being scattered inelastically must also be taken into account. An elegant theoretical description would treat the excitation and the transport of the excited electron through the solid as a one-step process. However, calculations of this type have not been carried out for such complicated systems as transition metals. Thus we are left with the widely used approximation of breaking the photoemission process up into independent steps thereby neglecting possible interference effects.

Before we focus on the energy region into which the $3p$-$3d$ resonances fall, a few remarks on the low-energy structures for Sc through Cr are in order. First, the in-

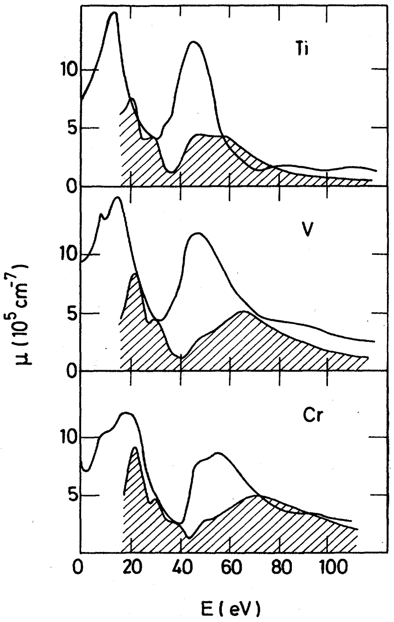

FIG. 3. Total-absorption cross sections of Ti, V, and Cr (from Ref. 17). The shaded area gives the partial $3d$ cross section from Fig. 2, normalized to the total absorption below the $3p$ threshold.

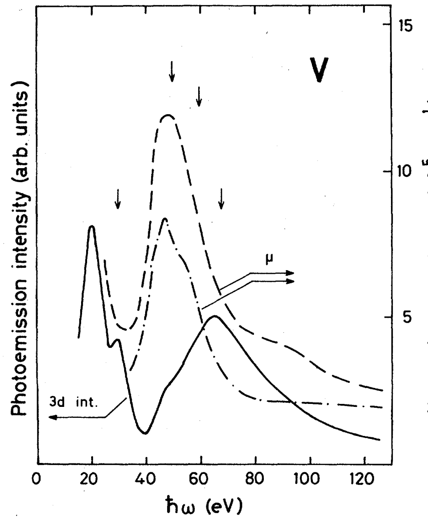

FIG. 4. Comparison between total-absorption cross sections obtained by direct-absorption measurement (dashed-dotted curve, Ref. 18) and calculated from energy-loss measurements (dashed curve, Ref. 17) for V. Note that the large discrepancy leads to a corresponding uncertainty when normalizing the $3d$ partial cross section to the total absorption. The vertical arrows refer to Fig. 6.

elastic mean free path of photoelectrons goes through a minimum for energies around 20 eV above the Fermi level which affects the $3d$ photoemission intensity at the corresponding photon energy.[8] Second, photoelectron surface refraction is expected to influence the $3d$ photoemission intensity for photon energies up to ~20 eV above threshold.[8] Also, surface reflection of the primary radiation will become prominent in this energy range. We did not study these effects systematically but it is likely that the prominent structures around 20-eV photon energy which appear in all $3d$ intensity measurements (see Fig. 2) originate from these effects since no comparable structures are discernible in the absorption spectra (Fig. 3). For the higher photon energy range the above effects will be much less important.[8] Note that the agreement between our photoemission yield spectra and the published absorption data in the region of the $3p$-$3d$ resonance absorption precludes explicitly any remarkable influence of surface reflection of the primary x-ray beam.

The $3p$-$3d$ "giant dipole resonance" dominates the absorption above the $3p$ thresholds and a large fraction of the $3p \rightarrow 3d$ resonance excitations is found in the $3d$ cross sections (Fig. 3). Coupling between the $3p \rightarrow 3d$ and the $3d \rightarrow \epsilon l$ excitations arises from the "super Coster-Kronig" decay of $3p^5 3d^{N+1}$ resonance states into the $3p^6 3d^{N-1}\ \epsilon l$ continuum.[21,22] This led Dietz *et al.*[23] and later Davis and Feldkamp[24] to apply Fanos theory to the $3p$ absorption spectra of the heavy $3d$ transition metals. The development of the $3p$ absorption resonances in the light $3d$ transition-metal atom was investigated by Mansfield and Newsom using a term-dependent Hartree-Fock calculation.[25] More elaborate models as the random-phase approximation[26] (RPA) or the time-dependent local-density approximation[27] (LDA) work out the detailed dynamics of the resonance interaction including the calculation of resonant photoemission cross sections. Specific calculations of the $3p$-$3d$ interaction are available for Cr (Ref. 28) and Ca (Ref. 29), both of which are basically atomic calculations modified, to simulate the situation in a solid. The $3d$ cross section for Cr was only calculated in a narrow energy range around the $3p$ threshold and does not permit conclusions on the detailed line shape of the $3d$ resonance profile.[28] For Ca the comparison between Wendin's calculation and our measurements is published separately.[30] It is found that theory and experiment show satisfactory agreement for the first, dominant maximum of the $3p$-$3d$ resonance in the $3d$ cross section but not for the additional structure on the high-energy side of the resonance, where the experiment shows a second well-resolved broad maximum coincident with the $3s$ threshold (compare Fig. 2). Although the calculation reveals a resonance in the $3d$ cross section due to the atomic $3s \rightarrow 4p$ excitation, this resonance does not appear to be sufficiently intense to give rise to the observed structure in the metal.[30] A $3s$-$3d$ coupling has recently been observed for metallic Ni,[31] but the corresponding feature in the $3d$ cross section is a weak and narrow window resonance which bears no resemblance to the broad intense maximum which we observe for Ca. It is thus concluded that the additional structure is most likely characteristic for the metal.

From Fig. 2 we recognize a regularity for the $3p$-$3d$ resonances of Ca through Cr (compare also Table I for the energy positions). Besides the structure in the $3d$ intensity which coincides with the maximum of the absorption resonance, the second maximum on the high-energy side develops and gradually gains in intensity relative to the intensity of the first maximum. The regularity suggests that there is a common origin for the additional maximum of all metals from Ca to Cr. It also corroborates the conclusion for Ca that the structure is not primarily due to a coupling to the $3s$ excitations since their oscillator strength is constant through this series, in contrast to the increasing relative intensity of the high-energy maximum of the $3d$ cross section.

To shed further light onto the suggested solid-state nature of the high-energy maximum we compare in Fig. 5 the $3d$ cross section of solid Cr (Ref. 7) to a measurement performed on a thin (~4 Å) Cr film evaporated onto a carbon substrate,[32] and to recently published data of Cr vapor.[33] The lower part of Fig. 5 contains the gross behavior of the vapor-phase $3d$ cross section in the vicinity of the $3p$-$3d$ resonance; finer details as to the coupling to weaker multiplet lines in the resonance have been omitted (compare Ref. 33). The results of the middle and upper part of Fig. 5 were obtained in a consistent way by integrating the $3d$ photoemission of EDC's taken at stepwise varied photon energies in the displayed energy region (for details see Ref. 7). Although such a data analysis leads to results which differ in some details from CIS spectra—the reason for this difference will be made clear below—the gross features obtained by either method agree. Thus Fig. 5 illustrates a dramatic change in the influence of the $3p$-$3d$ resonance on the $3d$ photoemission when going from gas-phase to solid-state Cr: The comparably sharp Fano resonance of the atom is washed out, and a second maximum at higher photon energies builds up for which the atom does not show any counterpart.

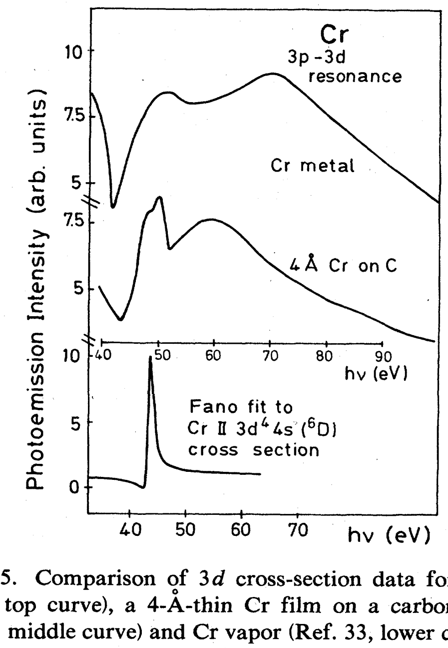

FIG. 5. Comparison of $3d$ cross-section data for Cr metal (Ref. 7, top curve), a 4-Å-thin Cr film on a carbon substrate (Ref. 32, middle curve) and Cr vapor (Ref. 33, lower curve). For the vapor only the gross behavior of the cross section is shown.

More detailed information about the $3p$-$3d$ resonances in the metal may be obtained from the energy distribution of the resonantly emitted photoelectrons. It may suffice to show our results for one example in which we choose V (Fig. 6). The filled part of its d band extends over ~3 eV, and the EDC's exhibit some details of the d-band density of states.[34] The EDC's in Fig. 6 are taken at several different photon energies, their location relative to the $3p$-$3d$ resonance is indicated by arrows in Fig. 4. The maximum intensity is fixed to enhance the visibility of the relative changes in the spectral intensity distribution. Thus it becomes evident that, while the d-band spectra for low (30 eV) and high (68 eV) photon energies agree up to 2-eV binding energy, there is a remarkable enhancement of the relative intensity from the higher binding-energy part of the d band when the photon energy is tuned to the giant absorption maximum (60 eV). This enhancement even extends to the binding energy region around 10 eV where the photoemission intensity would usually be attributed to the background of inelastically scattered electrons. Note that in this respect the 30-eV spectrum cannot serve as a good reference since here the higher binding-energy part of the spectrum is already severely distorted by the rise of intensity from inelastically scattered electrons towards 0-eV kinetic energy.

The shift in the relative photoemission intensity towards higher binding energies is observed in a photon energy region where the expectation of a maximum $3d$ ionization cross section due to the maximum of the $3p$-$3d$ giant absorption resonance is met with just a shoulder in the actual CIS spectrum of the top of the $3d$ band. This indicates that, for the decay of the $3p \rightarrow 3d$ resonance excitation, other final states other than single-hole band states must be taken into account.

Shake-up satellites of d-band excitations have been observed for Ni as weak, broad, though discernible, structures up to ~30-eV binding energy.[35] Apart from a maximum at 6 eV our EDC's do not indicate any noticeable structures which would allow a more specific interpretation of the final states for the decay of the $3p \rightarrow 3d$ excitations. Moreover, there is even no precise knowledge of the excited states themselves. Unlike the heavy $3d$ metals, the large width of the absorption resonances of the light $3d$ metals precludes an interpretation exclusively based on $3p^5 3d^{N+1}$ multiplet excitations.[24] XPS spectra of the V $3p$ electrons show a large satellite contribution (see Fig. 7) which cannot be explained by secondary energy losses of the photoelectrons.[36] Since these satellites cover the energy region up to the $3s$ level—as does the $3p$-$3d$ giant absorption resonance—and since some similarity between the final states may be assumed due to the $3d$ electron screening of the $3p$ hole in an XPS experiment,[37] we should consider that shake-up excitations may accompany $3p^5 3d^{N+1}$ multiplet excitations also in the absorption spectra. These states may then decay also into d-band shake-up satellites.

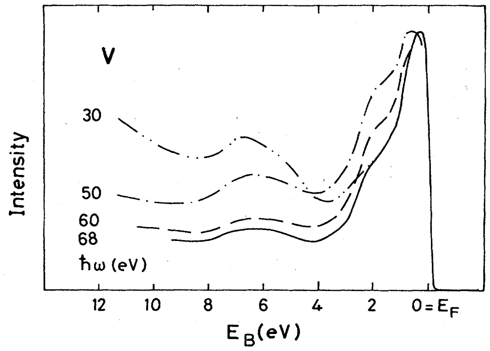

FIG. 6. Valence-band EDC's of V normalized to equal maximum intensity. The location of the selected photon energies relative to the $3p$ absorption resonance is indicated by the arrows in Fig. 4.

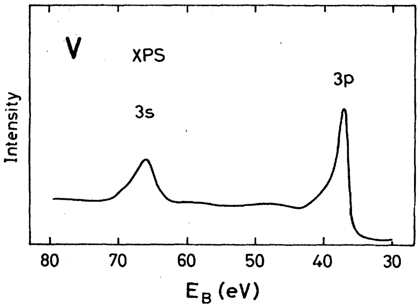

FIG. 7. XPS spectrum of V showing excitations accompanying the $3p$ photoemission (from Ref. 36).

Based on the above ideas we propose a model for the $3p \rightarrow 3d$ resonance excitations and their coupling to $3d$ valence excitations for the light $3d$ transition metals which are illustrated in Fig. 8. Figure 8(a) refers to the situation where the photon energy $\hbar\omega_1$ equals the nominal $3p \rightarrow 3d$ transition energy in a metal. The $3d$ valence electrons photoionized directly interfere with electrons ejected in a direct recombination decay of the $3p \rightarrow 3d$ excitations. In Fig. 8(b) the photon energy is larger than the nominal resonance energy, however, the same interference effect may still occur if the lifetime of the intermediate state is sufficiently short to spread the transition energy. In addition we may excite a $3p^5 3d^{N+1}$ shake-up satellite which leaves the solid in an excited ionized final state even after a direct recombination of the core hole. In Fig. 8 the shake-up excitation is represented by electron-hole pairs, but in principle, all excitations of the dielectric medium may serve as candidates. These excitations can be assumed to be mainly collective according to the interpretation of the dielectric function of the light $3d$ metals up to ~40 eV.[17]

Given the above model the following qualitative observations can be made.

(i) The dramatic change of the $3d$ resonant photoemission cross section between the free atom and the solid as displayed in Fig. 5 could be attributed to collective solid-state excitations interacting with the $3p \rightarrow 3d$ resonance excitations. This suppresses the first maximum in the $3d$ cross section close to the $3p$ threshold because of the resonant enhancement of a "background" of valence excitation satellites which are distributed continuously over binding energies of some 10 eV. The decreasing importance of collective excitations at higher energies (i.e.,

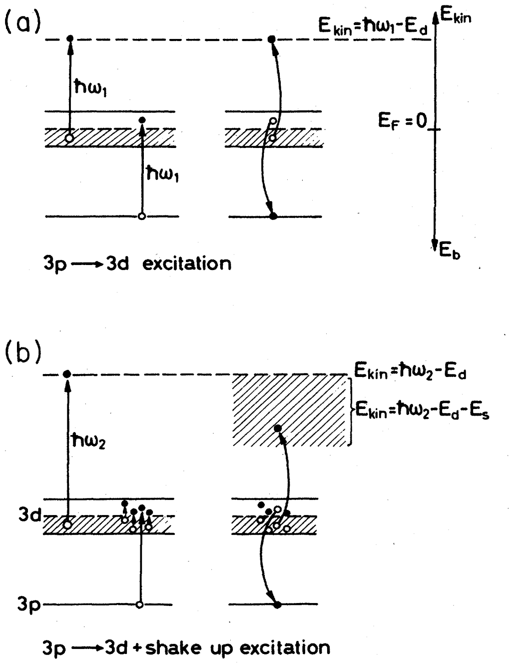

FIG. 8. Model for the $3p$-$3d$ intershell interaction. (a) refers to the interference between $3p$ and $3d$ excitations by direct recombination of $3p^5 3d^{N+1}$ intermediate states. (b) illustrates the direct recombination in the presence of additional shake-up excitations.

higher loss energies) is then responsible for the buildup of the high-energy maximum in the $3d$ resonance cross sections.

(ii) The trend in the relative strength of the first versus the second maximum in the $3d$ resonance cross sections (compare Fig. 2) may reflect an increasing number of available shake-up excitations probably due to the increasing d-band filling. The relative stability of the half-filled $3d$ shell in its atomic ground state which is present in Mn (not in Cr, compare Ref. 24) agrees with the observed similarity between the $3d$ resonance cross sections of Mn vapor[38] and the metal.[32]

(iii) The enhanced background of the $3d$ resonance photoemission which we attribute to shake-up satellites could explain the earlier finding for Cr that the summation of the cross sections of all one-electron final states does not reproduce the absorption cross section in the region of the resonance.[7]

III. COMPARISON WITH OTHER $3d$ CROSS-SECTION DATA

For the elements Ti and Cr comparable $3d$ cross-section measurements are available in the literature (Ref. 5 for Ti; Refs. 4, 7, and 39 for Cr). While there is agreement about the gross features as the resonance enhancement itself, it seems discouraging to find so little consistency in the details. On the other hand, this is not surprising in view of the different conditions under which the different cross-section measurements were performed. In some of the experiments, s polarized light was used to excite the sample (Refs. 4 and 7, this work), a mixture of s and p polarization was used in others (Refs. 5 and 39); some results were obtained from single crystals,[4,5,39] others from polycrystalline samples (Ref. 7, this work). Although these differences should not affect the excitation probability, they may influence inelastic scattering processes. Also the intensity of surface photoemission depends on these experimental parameters.[40]

Close attention should be paid to the angular distribution of the photoelectrons. For the atomic photoionization process this distribution is characterized by an energy-dependent asymmetry parameter which retains its meaning in the solid.[41] Photoelectron diffraction adds to the complexity of the angular distribution pattern.[41] Reliable data for partial subshell cross sections can thus only be obtained by collecting photoelectrons in a large solid angle. An angle resolved photoemission setup as used in Ref. 4 is least acceptable in this respect. The collection geometry of the experiment which was used in the present study has been described in detail elsewhere.[8] It essentially averages the photoemission over all polar angles; the polycrystalline nature of our samples ensures further that angular anisotropies have little influence on our evaluation of photoionization cross sections. Nevertheless, an uncertainty of 20—30% must probably still be assumed for the result. For the future it may be hoped that experimental conditions and data analysis procedures will allow a more reliable intercomparison of cross-section determinations.

In conclusion, we have presented a systematic study of the $3p$-$3d$ intershell interaction in metallic Ca through Cr. The results provide fundamental insight into the dynamics of the photoemission process in these metals. On the other hand, there is a high demand for photoionization cross-section data as a basis to interpret photon stimulated desorption[3] and electron-excited Auger[2,6] spectra both of which contain the fingerprints of intershell interaction. It may be recalled in this context that a complete analysis of "resonance recombination lines" in electron-excited Auger spectra, including peak position and line shape, is only possible if the corresponding partial photoionization cross sections are known.[42]

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