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THEORY OF RESONANT PHOTOEMISSION SPECTRA OF 3d TRANSITION METAL
OXIDES AND HALIDES

by

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Theory of Resonant Photoemission Spectra of 3d Transition Metal

Oxides and Halides

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A b s t r a c t

A simple model is presented to describe resonant photoemission due to super-Coster-Kronig decay of $3p^5 3d^{N+1}$ states in transition metal compounds. An explanation is given for the puzzling behavior observed in recent experiments on NiO and NiCl₂ in which the multi-electron satellite is enhanced rather than the main valence band. Several experiments are proposed to test the theory.

* Work done while author was a guest scientist at the Deutsches Elektronen-Synchrotron, 2000 Hamburg 52, BRD.

The UPS and XPS spectra of the valence bands of 3d transition metal oxides and halides have usually been interpreted in terms of ligand field theory.^{1,2,3} The principal emission is identified with the crystal field multiplets of the $3d^{N-1}$ configuration of the metal ion.⁴ However, recent resonant photoemission experiments on NiO⁵ and the series XCl₂, X = Ni, Co, Fe, and Mn,⁶ show that this interpretation cannot be entirely correct. The resonance involves the excitation of the metal 3p core level giving discrete excited states with configuration $3p^5 3d^{N+1}$ which decay via super-Coster-Kronig (sCK) processes⁷ to $3p^6 3d^{N-1}$ of final continuum states. These should be the same final states as excited by direct emission from the valence bands. Hence, we expect the resonance to occur in the main 3d lines. Instead, experiment shows enhancement in the Ni compounds of the so-called multielectron satellite in conflict with the simple ligand field interpretation. For MnCl₂, the resonant enhancement is mostly in the main 3d emission while FeCl₂ and CoCl₂ show intermediate behavior.

From the work of Larsson and Braga⁸ and of van der Laan et al.,⁹ it has become clear that core level XPS spectra, which often show strong shake-up satellites,¹⁰ can only be understood, if the hybridization of the 3d levels with the ligand levels is accounted for. Following these ideas, the purpose of the present work is to present a simple model for the effect of 3d-ligand interactions of the valence band spectra, particularly to explain the resonance phenomena. Understanding the behavior of these compounds is important, because of the intrinsic interest in their electronic properties and because they can serve as models for the investigation of more complicated materials.

The Hamiltonian for the calculations presented in this paper is

$$H = -\epsilon_d \sum_{\sigma} d_{\sigma} d_{\sigma}^{\dagger} - \epsilon_L \sum_{\sigma} c_{\sigma} c_{\sigma}^{\dagger} - T \sum_{\sigma} (d_{\sigma} c_{\sigma}^{\dagger} + c_{\sigma} d_{\sigma}^{\dagger}) + U d_{\downarrow} d_{\downarrow}^{\dagger} d_{\uparrow} d_{\uparrow}^{\dagger} \quad (1)$$

where the operator d_{σ}^{\dagger} creates a 3d electron of spin σ and energy ϵ_d on the metal ion, while c_{σ}^{\dagger} creates an electron in an orbital of the same symmetry made up of ligand basis functions of energy ϵ_L . The meaning of ϵ_d and ϵ_L will be made more precise below. The mixing of these levels is represented by T and U is the 3d hole-hole Coulomb repulsion. Since the ligand

orbital is not so localized, the ligand-ligand Coulomb interaction is neglected. For simplicity, the orbital degeneracy of the levels is also neglected.

In the ground state, let us assume there is only one hole. This is the simplest non-trivial case to consider. The wave function is

$$|\psi_g\rangle = (\cos \theta d_{\downarrow} + \sin \theta c_{\downarrow})|\Phi\rangle, \quad (2)$$

where $|\Phi\rangle$ represents completely filled levels. Substituting (2) into (1) we find

$$\tan \theta = T/(\Delta + \sqrt{\Delta^2 + T^2}), \quad (3)$$

where

$$2\Delta = \epsilon_d - \epsilon_L. \quad (4)$$

For $\epsilon_L \ll \epsilon_d$, $\theta \rightarrow 0$ and $|\psi_g\rangle$ corresponds to a single hole in the 3d level, i.e. the configuration \underline{d} (a bar under d or L indicates a hole in the respective levels). On the other hand, for $\epsilon_L \gg \epsilon_d$ the ligand level is unoccupied. For $|\Delta| \ll T$ (we can take $T > 0$ without loss of generality), the hole is shared by the metal ion and the ligand. In Fig. 1a, the dependence of $\cos \theta$ and $\sin \theta$ on ϵ_L is shown for some typical parameters.

Valence band photoemission introduces an additional hole. The simplest of the two-hole states are the triplet states ($S=1$), where $|\psi\rangle = d_{\downarrow} c_{\uparrow} |\Phi\rangle$ for $M_S = -2\sigma$ and $\frac{1}{\sqrt{2}}(d_{\downarrow} c_{\uparrow} - c_{\downarrow} d_{\uparrow})|\Phi\rangle$ for $M_S = 0$. The energy is $E = -\epsilon_d - \epsilon_L$. Only the singlet states involve the Coulomb repulsion U and the mixing T . They are of the form

$$|\psi\rangle = \alpha(d_{\downarrow} c_{\uparrow} + c_{\downarrow} d_{\uparrow})|\Phi\rangle + \beta d_{\downarrow} d_{\uparrow}|\Phi\rangle + \gamma c_{\downarrow} c_{\uparrow}|\Phi\rangle \quad (5)$$

Substituting (5) into (1), we obtain the eigenvalue equations

$$\begin{aligned} (E + \epsilon_d + \epsilon_L)\alpha + T\beta + T\gamma &= 0, \\ 2T\alpha + (E + 2\epsilon_d - U)\beta &= 0, \\ 2T\alpha + (E + 2\epsilon_L)\gamma &= 0. \end{aligned} \quad (6)$$

Eq. (6) can be solved simply by numerical means. Let us first, however, examine some limiting cases.

If $\epsilon_L \ll \epsilon_d - U$, the lowest energy solution corresponds mostly to the \underline{d}^2 configuration ($\beta=1$) with $E \approx -2\epsilon_d + U$, i.e. two d holes. The highest energy solution is mostly \underline{L}^2 ($\gamma=1$) with $E \approx -2\epsilon_L$ and the middle solution is $\sim \underline{d} \underline{L}$ ($\alpha \approx 1/\sqrt{2}$) with $E \approx -\epsilon_d - \epsilon_L$. In this case, the ligand levels have large binding energy and crystal field theory describes the d states well.

For $\epsilon_L = \epsilon_d - U$, the $\underline{d} \underline{L}$ and \underline{d}^2 configurations become degenerate and the two lowest energy solutions are linear combinations of these ($2\alpha^2 = \beta^2 = 1/2$). Likewise, at $\epsilon_L = \epsilon_d - \frac{1}{2}U$, \underline{L}^2 and \underline{d}^2 are degenerate and combine to form the two highest energy solutions. For $\epsilon_L \gg \epsilon_d - \frac{1}{2}U$, the highest energy solution has mainly the \underline{d}^2 configuration.

In Fig. 1b, the coefficients α , and β , of the lowest energy solution are shown as a function of ϵ_L . For $\epsilon_L \gg \epsilon_d$, α , and β , $\rightarrow 0$ and γ , (not shown) approaches unity.

To make the meaning of ϵ_d and ϵ_L clearer, we consider the model in the absence of mixing ($T=0$) and for $\epsilon_L < \epsilon_d$. The ground state is then \underline{d} . The amount of energy required to remove a ligand electron is $-\epsilon_L$ and a 3d electron is $-\epsilon_d + U$. Therefore, these are the binding energies in this limit. On the other hand, the energy to transfer an electron from the ligand to the metal ion is $\epsilon_d - \epsilon_L$, so $-\epsilon_d$ can be regarded as the electron affinity of the metal ion. The relative binding energies of the ligand and 3d levels determine the final states, whereas the metal ion electron affinity and the ligand binding energy determine the ground state (along with T).

The photoemission intensity from the triplet states can be shown to be $3/2 \sin^2 \theta$ (in units of $\frac{2\pi}{\hbar} \langle \epsilon \ell | \vec{r} \cdot \vec{E}_0 | 3d \rangle^2$). We include only dipole matrix elements between 3d and the continuum orbital $\epsilon \ell$, neglecting any ligand emission. The discrete excited state representing the $3p \rightarrow 3d$ transition has configuration \underline{p} (full valence levels). Let us assume that only sCK decay to the \underline{d}^2 configuration is allowed. Then there is no resonant enhancement of the triplets states, because they do not contain \underline{d}^2 .

The emission from each of the singlet states (labeled by index k) is given by⁷

$$N_k = |\alpha_k \sin \Theta + \beta_k \cos \Theta \frac{\epsilon + q}{\epsilon + 1}|^2, \quad (7)$$

$$\epsilon = \frac{h\nu - h\nu_0}{\Gamma}, \quad (8)$$

where $h\nu$ is the photon energy and $h\nu_0$ is the resonance energy, $2\Gamma = 2\pi V_{sCK}^2$ is the sCK decay width (FWHM), and the Fano asymmetry parameters

$$q = \frac{\langle 3d | \vec{r} | 3p \rangle}{\pi V_{sCK} \langle \epsilon l | \vec{r} | 3d \rangle}. \quad (9)$$

The total singlet emission away from resonance ($|\epsilon| \rightarrow \infty$) is $\cos^2 \Theta + \frac{1}{2} \sin^2 \Theta$. The sum of singlet and triplet emission is $\cos^2 \Theta + 2 \sin^2 \Theta$ which equals the number of d electrons in the ground state.

The off-resonance photoemission spectra are shown in Fig. 2. For $\epsilon_L \ll \epsilon_d$, the ground state is \underline{d} ($\sin \Theta \approx 0$) and consequently the intensity distribution is determined solely by the \underline{d}^2 amplitude β_k of the final state, i.e. the $\underline{d} \rightarrow \underline{d}^2$ process. For $|\epsilon_d - \epsilon_L| \ll \Gamma$, the ground state contains a \underline{L} component as well as a \underline{d} component. In this case the intensity is determined by $\underline{L} \rightarrow \underline{d} \underline{L}$ and $\underline{d} \rightarrow \underline{d}^2$ processes.

The resonant behavior is depicted in Figs. 3 and 4. The emission of the three singlet states as a function of photon energy is plotted for different ϵ_L . Since the discrete state has configuration \underline{p} , the resonant portion of the amplitude for photoemission depends only upon the \underline{d}^2 component (only β_k appears in the term containing $\frac{\epsilon + q}{\epsilon + 1}$ in Eq. 7, not α_k or γ_k). The strength of the resonance depends upon the amount $\cos \Theta$ of d hole in ψ_g , since only metal $3p \rightarrow 3d$ transitions are important, not $3p \rightarrow L$.

For $\epsilon_L \ll \epsilon_d - U$, the lowest energy solution contains mostly the \underline{d}^2 configuration. We see from Fig. 3 that the resonant enhancement is predominantly in this line (N_1). As remarked previously, this behavior is expected when simple ligand field theory is valid and ligand excitations themselves

are unimportant. As ϵ_L is increased (less negative relative to ϵ_d), the resonant enhancement shifts to the higher energy solutions. For the region of ligand energy, where $\epsilon_L \approx \epsilon_d - T$, the behavior is qualitatively similar to the experimental results^{5,6} for NiO and NiCl₂. In these compounds, the off-resonant emission is mostly at low binding energy (main lines). However, the resonance occurs principally in the satellite with the main lines showing an interference dip⁷. In the model, this effect is possible, since the resonant process enhances different final states than those excited directly when the ground state is hybridized. Mixing in the final states alone does not give the proper behavior.

To apply these concepts to actual compounds, we must generalize the model. For a compound which is nominally d^N in the ground state, $\psi_g = \cos \Theta d^N + \sin \Theta d^{N+1} \underline{L}$. Presumably other configurations do not contribute strongly. The final states are of the form $\alpha d^N \underline{L} + \beta d^{N-1} + \gamma d^{N+1} \underline{L}^2$. The multiplet structure in the $3p$ absorption¹¹ and yield⁶ spectra indicate that the dominant configuration in the discrete excited states is $p^5 d^{N+1}$. These decay via sCK transitions to the d^{N-1} configuration. The resonant process therefore enhances final states with a large β coefficient (large d^{N-1} component) whereas the direct emission is from states for which $|\beta \cos \Theta + \alpha \sin \Theta \eta|$ is large. η is a factor due to the different amplitudes for emission from d^N and d^{N+1} . In general these will not be the same states.

There may also be some emission from the ligand levels which could contribute to the valence band intensity.

If $\sin \Theta$ is small (little mixing in the ground state), we expect the resonant enhancement to occur in those final states excited directly. NiF₂ may be such a case. Apparently¹² it has little ground state hybridization (nearly pure d^8), because of the large electronegativity of F. If this is true, these considerations imply that the main valence band emission should be resonantly enhanced (similar to MnCl₂) in contrast to NiO and NiCl₂ where the satellite is enhanced. This would make a nice experimental test of the ideas presented here and the analysis given by Zaanen and Sawatzky.¹²

Another interesting example for a resonant photoemission experiment is the Cu dihalide series (CuX₂, X = F, Cl, Br and I). The ligand binding energy varies systematically with little change in other parameters.¹² The series

has simple configurations and multiplets. The discrete excited states can only have the configuration $3p^5 3d^{10}$, since the valence levels contain a single hole in the ground state. The analysis should be a straight forward extension of the present work and of Ref. 9.

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Figure Captions

- Fig. 1 (a) Coefficients of the d-hole ($\cos \Theta$) and ligand-hole ($\sin \Theta$) components of the ground state versus ligand energy ϵ_L . (b) Coefficients of the configuration with a d-hole and a ligand hole (d_1) and with two d-holes (β_1) in the final state with the lowest binding energy. Normalization is $2\alpha_1^2 + \beta_1^2 + \gamma_1^2 = 1$. $\epsilon_d = 0$, $T = 2$ and $U = 8$. All energies are in eV.
- Fig. 2 Off-resonance photoemission spectra for various ligand energies ϵ_L . Triplet final states are denoted by $S = 1$ and the singlet states by N_R . Total intensity is $\cos^2 \Theta + 2 \sin^2 \Theta$. Parameters same as in Fig. 1.
- Fig. 3 Photoemission intensity of singlet final states as a function of photon energy relative to resonance. Triplet states are not resonantly enhanced. $\Gamma = 1$, $q = 1.5$ and other parameters same as Fig. 1.
- Fig. 4 Same as Fig. 3 for smaller ligand binding energies.

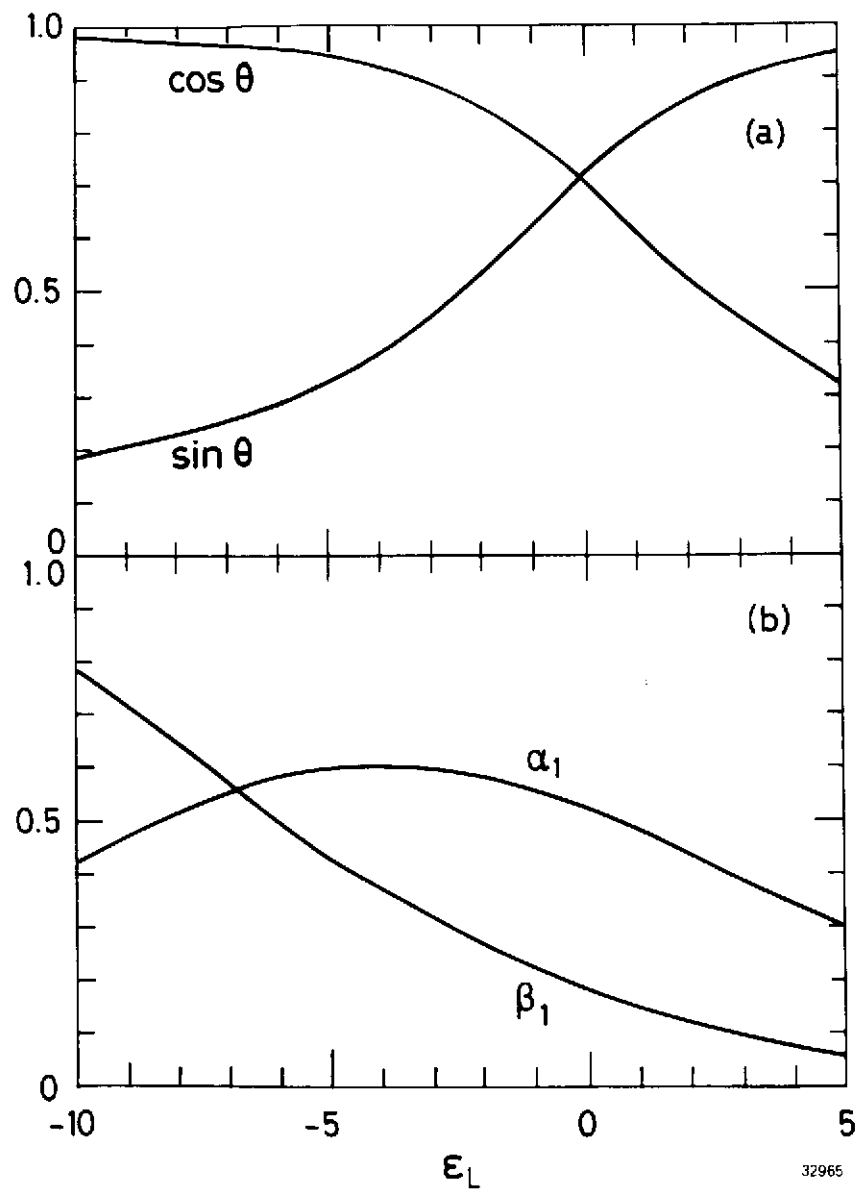


Fig. 1

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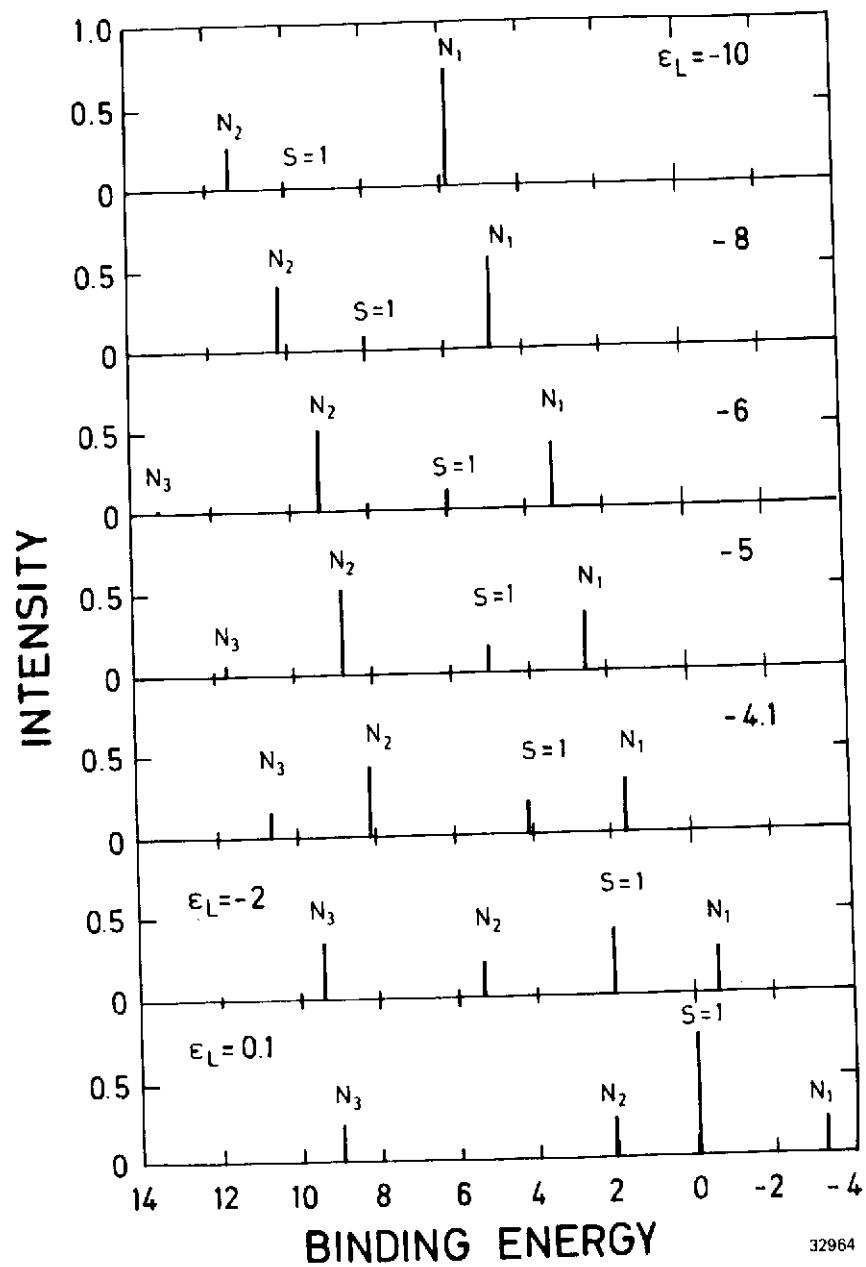


Fig. 2

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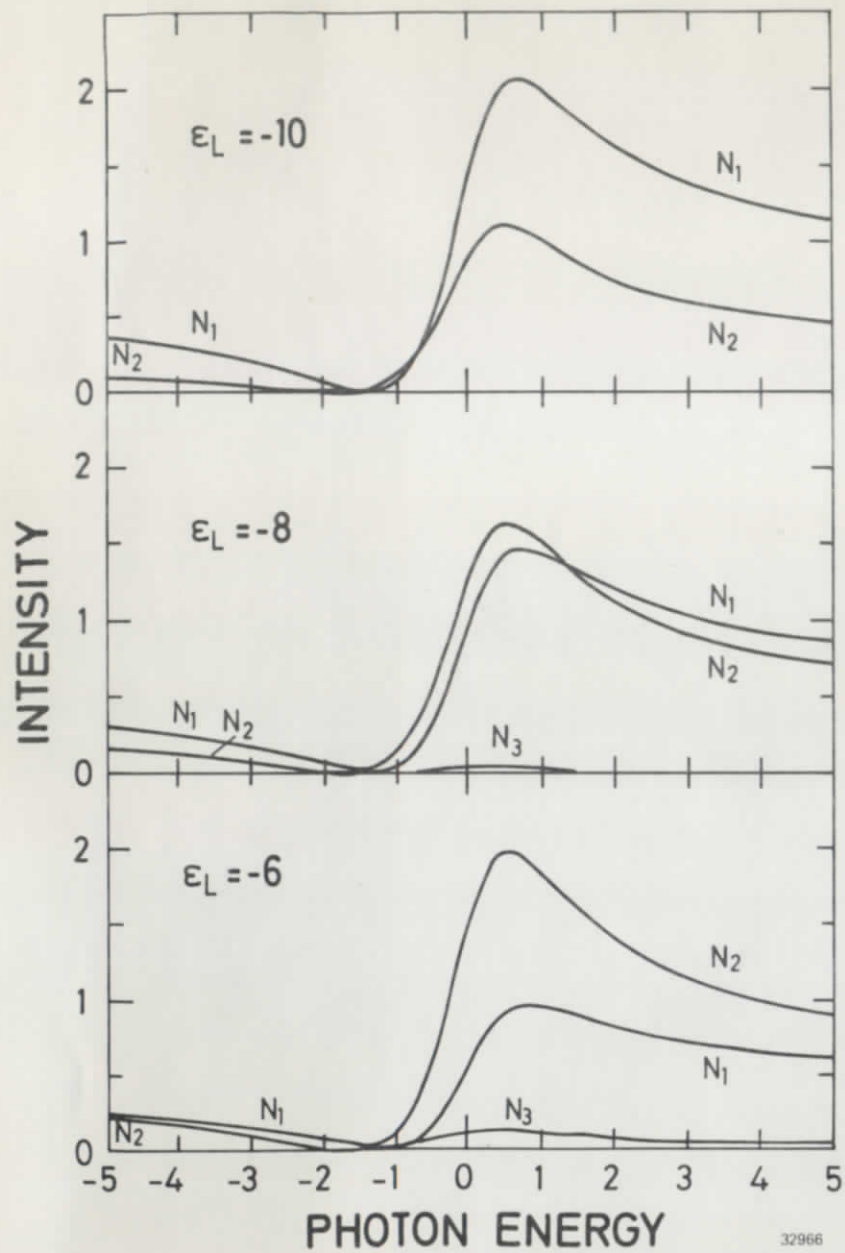


Fig. 3

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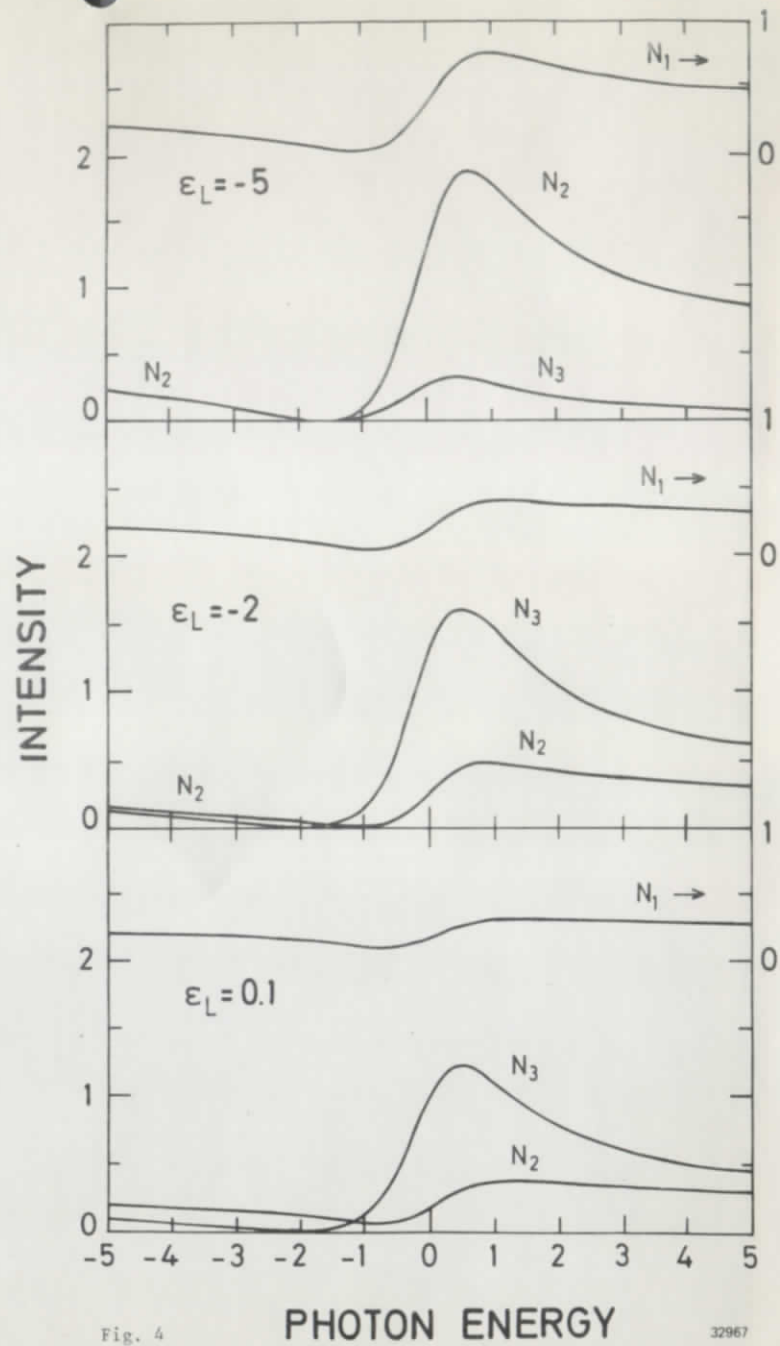


Fig. 4

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