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RESONANT PHOTOEMISSION AT THE 3p-CORE THRESHOLD FROM QUASIATOMIC Ni IN NICKEL-PHTHALOCYANINE

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Resonant Photoemission at the 3p-Core Threshold from Quasiatomic Ni in Nickel-Phthalocyanine[+]

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In Nickel-Phthalocyanine a resonant enhancement at the 3p - Ni photoabsorption maximum ($h\nu = 68.5$ eV) of a peak approximately 6 eV below the maximum of the Ni 3d derived states is observed in photoemission experiments with variable excitation energy (synchrotron radiation). Our observation of this resonance, explained by configuration interaction of Ni 3p → 3d and 3d - continuum transitions, gives direct evidence for the atomic nature of the 6 eV resonance structure in photoemission from bulk Ni.

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In metal phthalocyanines (PC's) the central metal atom replacing the two H atoms of the metal free PC is surrounded in a quasi-matrix by well defined ligands of low atomic weight (see insert in Fig. 1). The bonding is in most cases covalent[1]. Recent photoemission experiments with variable photon energy have shown[2] that the gross features of the partial cross section dependence of the outer metal core levels can be described in an atomic picture supporting the model of a metal atom in a matrix. By measuring the photoelectron energy distribution curves (PED's) from both, the metal- and the metal-free-PC, difference spectra emphasizing the contributions of the metal atoms to the valence band density of states can be obtained[3]. Experimentally this method applied to metalorganic materials where a few metal atoms are dispersed in a quasi-matrix is analogous to the difference PED curves in photoemission experiments from adsorbates. We note in passing that an assessment of the differences in the PED-curves from metal free- and metal-PC's by visual inspection has been applied for a number of PC's in the solid phase[4] and recently also for the gas phase[5].

In the present paper we report on photoemission experiments on Ni-Pc and H_2-Pc which reveal a resonant enhancement of a valence band peak in Ni-Pc ≈ 6.1 eV below the maximum of the Ni 3d density of valence states for photon energies around 68 eV. This resonance is absent in H_2-Pc. We interpret this enhancement as a resonant photoemission of quasiatomic Ni caused by a configuration interaction between Ni 3p → 3d and continuum transitions. Our result strongly supports an atomic interpretation of the resonant enhancement of the "6eV-peak" in Ni-metal observed recently for the same photon energies by Guillot et al.[6].

For Ni-metal many attempts have been made in order to understand the structure of the 3d-bands and the peak which is located approximately 6 eV below the Fermi edge[6-15]. The interpretation of this feature remains controversial until now. Kemeny and Shevchik[12] have pointed out, that this peak may have the same origin as the satellite structure in the XPS-spectra of the 2s, 3s and 3p levels[9] because of the very localized character of the Ni-3d electrons. This interpretation is based on the theory of Kotani and Toyozawa[8]. Another explanation has been proposed by Smith et al.[13], who are pointing out, that the 6eV peak is consistent with a band structure picture for transitions associated with a s-p band. Basically this view point has recently been corroborated by Eastman et al.[15] for a (111) surface of a Ni crystal. These authors explained, based on the dispersion observed in detailed angular resolved photoemisssion experiments, the 6eV peak off resonance as due to transitions from the s-p derived Ni valence band Λ_1.

Experiments by Tibbetts and Egelhoff[7] on Ni vapor, deposited on an amorphous carbon substrate, suggested that the origin of the 6eV-peak has a dominant atomic character. The photoemission experiments by Guillot et al.[6] using continuous synchrotron radiation show a strong resonance enhancement of the 6eV feature due to coupling of the quasidiscrete 3p → 3d transition with continuum states in the photon energy region between 63 eV and 73 eV. As these authors pointed out, the "6 eV peak" off resonance and the resonance must have a different physical origin.

In order to clarify this situation photoemission experiments from atomic Nickel at the same photon energies would be highly desirable. In view of the apparent difficulties of such experiments we have investigated Ni in a quasi-atomic state, namely in a PC-matrix.

Polycrystalline thin films approximately 200 Å thick have been used as samples. They were sublimed onto a stainless steel substrate from purified powder (Eastman and Kodak). The molecular structure of the compound is sketched in the insert of Fig. 1. In solid Ni-PC the minimum Ni-Ni distance is 4.7 Å[16], which is about two times larger than in the metal phase. Furthermore, the particle density of Ni in Ni-PC is by a factor of about 50 smaller

than in the metal. Our photoemission experiments were performed at the Synchrotron Radiation Laboratory at the DORIS storage ring in Hamburg. Synchrotron radiation was monochromatized with the grazing incidence monochromator FLIPPER[17]. A commercial double pass cylindrical mirror analyser was used as the electron analyser. In general, an overall resolution of 0.5 eV was sufficient for the observed structures in the PED's.

A selection from a family of PED curves for Ni-Pc in the range of photon energies between 63 eV and 152 eV is displayed in Fig. 1. The binding energy scale E_B is referrred to the vacuum level $E_V \equiv 0$. Spectra up to $h\nu = 75.9$ eV have been normalized in intensity at $E_B \approx 24$ eV. This normalization is justified in view of the cross-section measurements by Iwan et al.[2], which show a nearly constant intensity in this energy range. We note that different normalisation procedures gave essentially the same results. Spectra obtained with smaller photon energies show the same shape as the spectrum at $h\nu = 63.5$ eV. For photon energies $h\nu \gtrsim 100$ eV the Ni 3d derived valence states are strongly emphasized (see below). A spectrum of metal-free phthalocyanine (H_2-PC) at $h\nu = 151.6$ eV is shown in Fig. 2 in comparison to Ni-PC. Note, that this spectrum for H_2-PC is very similar to those from Ni-PC for $h\nu \lesssim 63.5$ eV.

From the spectra in Fig. 1 it is evident, that there is a strong resonance at $h\nu = 68.5$ eV and to a smaller extend at $h\nu = 69.9$ eV at binding energies around 13 eV. In addition to the resonant enhancement there occurs a shift in binding energy for peak D of $\approx$ 0.5 eV. This apparent shift is caused by a superposition of the resonance feature and the peak D originating from PC derived valence orbitals[2-4]. Since no similar enhancement was observed in the same energy region in PED's from other PC's (e.g. H_2-PC, Mg-Pc and Pb-PC), we can associate the enhancement unambiguously with the central Ni - atom. The magnitude of the resonance has been estimated by comparing the spectrum at $h\nu = 68.5$ eV and $h\nu = 69.9$ eV with with spectra obtained off-resonance at $h\nu = 65.9$ eV and 72.8 eV (shaded area in Fig.1). The resonant enhancement is a fairly large effect in view of the 1 : 50 dilution of Ni atoms in Ni-Pc as compared to bulk Ni and the large background signal due to PC-derived valence states with the same binding energies.

Next we try to locate the resonance peak with reference to other known features in the valence band density of states in the PED curves. Using the known Ni 3d - cross section dependence on hν we can easily identify the Ni - 3d contribution to the PED curve at hν = 151.6 eV. For these photon energies the Ni - 3d cross section is an order of magnitude larger than for hν ≈ 65 eV. Thus the appearance of a new peak with increasing photon energy on the low energy side of feature B is associated with the Ni - 3d contribution. A quantitive measure of the extend of this 3d - contribution to the density of valence states is obtained by taking the difference spectrum between Ni - Pc and H_2 - Pc spectra. For hν = 151.6 eV this difference spectrum is shown by the dashed line in Fig. 1 and in more detail in Fig. 2. In Fig. 2 we also compare this difference curve with a difference spectrum obtained by Tibbetts et al. for 0.2 Å Ni on a carbon substrate[7] and with an angle integrated PED curve for a thick solid Ni film. From this comparison it is evident that the difference curve reflects Ni-features. The maximum of these Ni - 3d derived states is separated from the Ni-Pc valence band feature B by about 1.3 eV and more important from the resonance feature observed at hν = 68.5 eV by 6.1 eV (Fig. 1).

Our results for quasi-atomic Ni resemble closely the observations for Ni-metal[6], with the important consequence that the resonance of the 6 eV peak for bulk Ni is a strongly localized atomic effect. Thus our experiment seems to be the first experimental verification of this hypothesis. In the following we discuss the nature of the "6eVpeak" and the resonance in some more detail.

First we note that in both, our difference curve ΔN(E) and the spectra by Tibbetts et al.[7] the separation of the Ni - 3d derived maximum and the "6eVpeak" is about 4.5 to 5.0 eV (Fig. 2) whereas the resonance feature has a larger separation of 6.1 eV from the 3d maximum. This 1 eV difference shows that two different processes contribute to what is vaguely termed the "6 eV peak".

Next we discuss the nature of the resonance. As known from electron spin resonance data the ground state of the Ni - atom in Ni-PC can be written as $3p^6\ 3d^8\ 4s^2$ (Ref 1). Mostly the two s-electrons are involved in bonding to the ligands and their spatial density at the Ni site is about 50 %[1]. Thus we can assume approximately a $3p^6\ 3d^8\ 4s^2$ ground state configuration in the molecular environment. (Note that in Ni-metal the configuration is closer to $3p^6\ 3d^9\ 4s$.) The origin of the resonance is a Fano-type interaction[18] of a quasidiscrete state with continuum states[6]. If the photon energy reaches the maximum for 3p - absorption at around 68 eV[19] the following transition can occur (neglecting 4s electrons):

$$3p^6\ 3d^8 + h\nu \rightarrow 3p^5\ 3d^9$$

This intermediate state is coupled with the 3d - continuum via autoionization (Super Coster-Kronig transition):

$$3p^5\ 3d^9 \rightarrow 3p^6\ 3d^7 + \text{free electron}$$

This kind of process has recently been observed and discussed in a number of cases, where resonance enhancements in photoemission have been observed (bulk Ni[6,20]; in rare earth compounds, 4d → 4f[20,21,22]; and in Ce[20,23] 4d → 4f). Except for Ni, the authors of these investigations point out that the resonance enhancement occurs within the respective valence band density of states and in fact have used the enhancement in order to locate hidden partial density of states[20,21,23].

For Ni we have shown that the resonance is of atomic nature and occurs far outside the 3d valence band density of states, which has a width of about 3.4 eV[15]. The explanation for the resonance on the basis of a simple Fano-type configuration interaction given above and proposed already for bulk Ni by Guillot et al.[6] seems to explain only part of the phenomenon. The question why there is no resonance observed for the main 3d features is still a standing problem. Thus caution should be exercised in using the resonance enhancement for a location of hidden energy bands as proposed e.g. in Ref. 20,21 and 23.

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Figure captions

Fig. 1 For Ni-Phthalocyanine the resonance enhancement at hν = 68.5 eV is shown in a set of photoelectron energy distribution curves obtained with various photon energies. The insert gives the molecular structure of Ni-Pc (full circles indicate N-atoms while the rest of the framework is built up by C and H-atoms). The binding energy scale is referred to the vacuum level $E_{VAC} = 0$.

Fig. 2 Photoelectron energy distribution curves for H_2-PC and Ni-PC at hν = 151.6 eV are shown in the upper part. Counting rates have been setequal at $E_B \sim 25$ eV where no pronounced valence band structure is observed. The difference spectrum (Ni-Pc minus H_2-Pc) ΔN(E) (middle part) is compared to a difference curve of Ni-atoms dispersed on a carbon substrate[7] obtained with hν = 40.8 eV. The lower panel shows the result for an evaporated solid Ni-film[7]. The binding energy scales for the upper and middle panel refer to $E_{VAC} \doteq 0$. For the lower panel the d-band maximum has been alligned with the ΔN curves. Note that in ΔN(E) there is also a small contribution at around E_B = 16 eV which is real but admittedly with larger error bars.

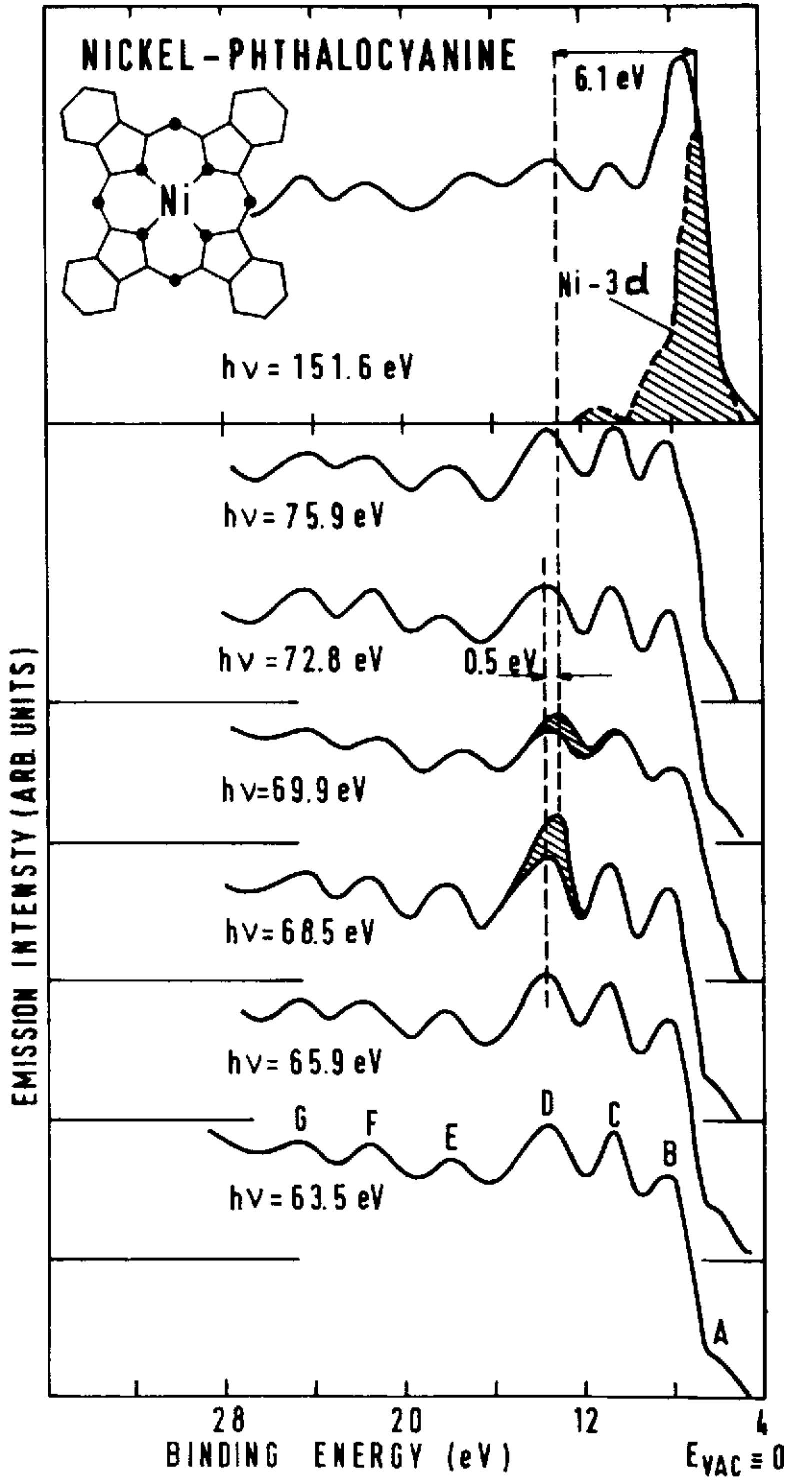

Fig. 1

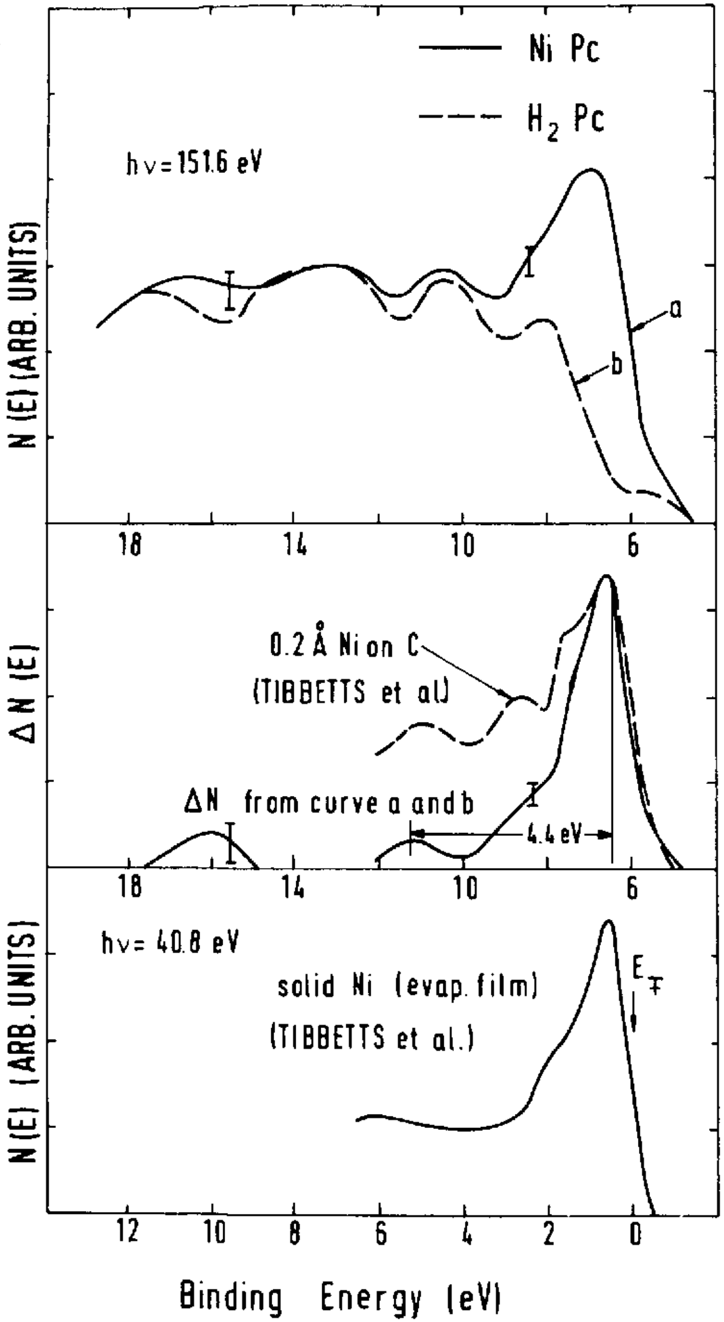
Ni Pc
H2 Pc
hν=151.6 eV
a
b
N (E) (ARB. UNITS)
18
14
10
6
Δ N (E)
0.2 Å Ni on C
(TIBBETTS et al)
ΔN from curve a and b
4.4 eV
18
14
10
6
hν= 40.8 eV
solid Ni (evap. film)
(TIBBETTS et al.)
E_F
N(E) (ARB. UNITS)
12
10
8
6
4
2
0
Binding Energy (eV)

Fig. 2