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ROLE OF MULTIELECTRON EXCITATIONS IN THE L3 XANES OF Pd

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High resolution L_3 and L_2 XANES (X-ray absorption near edge structure) spectra of Pd metal have been measured at the Frascati synchrotron radiation facility. The L_3 XANES shows an intense $2p \to 4d$ "white line" while at the L_2 a weaker structure appears. A good agreement between L_3 XANES and the one-electron theory of Muller et al. has been found. All the possible final state effects due to the relaxation of the many body system are discussed. No many body effects have been seen on the "white line" at threshold. The intensity ratio between L_3 and L_2 absorption is 2.1 in the high energy range of XANES and it is 2.7 at the white line maximum. A weak broad band extending up to 13 eV and centered at ~ 6 eV above the Fermi level, appearing in the L_3-L_2 difference spectrum, could be tentatively assigned either to the only possible very weak multielectron excitaton present in XANES of Pd i.e. the "two hole-two electron" excited state or to the prevalence of the $j=5/2$ total angular momentum for electrons in the 5sp band, hybridized with the 4d band, up to 13 eV above the Fermi level.

INTRODUCTION

The actual interest on XANES (X-ray absorption near edge structure) [1-3] is due to its capability to give unique direct information on local structure of complexes [1], surfaces [2], and proteins [3]. The experimental evidence that the XANES is determined by the local structure [1-3] is related to the explanation of XANES as multiple scattering resonances of excited photoelectron by neighbour atoms predicted by one-electron theories [4-6]. These theories do not take account [6] or take account [4] of final state effects only by assuming a static final state potential with one electron removed from the core level, in agreement with the von Barth and Grossman rule [7].

The presence of many body final state effects, due to the rearrangement of the rest of the electrons (passive electrons) in the atom and in the surrounding environment following the core hole excitation, can induce changes in the lineshape and give new satellite features which deserves accurate experimental investigation, to determine the relevance of final state effects in XANES.

We have focussed our interest on the "white line" which appears in the L_3 XANES of palladium like in transition metals [8-11] and rare earth compounds [12]. Recently it has been pointed out that these "white line" provide a novel method for probing:
a) the change in the number of empty d holes in transition metal catalysts [11]
b) the total angular momentum character $j = \ell \pm 1/2$ of empty conduction band states [13]
c) the "intermediate valence" in mixed valent rare earth compounds [12].

II. EXPERIMENTAL

The experiment has been carried out, using a vacuum beam line, at Frascati Laboratories using the storage ring ADONE operated at low energy 1.2 GeV to suppress the third harmonic content at 3 KeV photon energy. We have used a 100 μm horizontal exit slit on the Si(111) channel cut monochromator to obtain high resolution spectra $\Delta E/E = 1.3 \times 10^{-4}$ determined by the rocking curve of the crystal.

III. XANES AND ITS ONE-ELECTRON INTERPRETATON

Fig.1 shows the L_3 and L_2 XANES of palladium metal. The intensity ratio L_3/L_2 is 2.1, at high energies above threshold, close to the statistical weight of the initial states, but a large deviation $L_3/L_2 = 2.7$, is observed for the white line intensities at threshold. The L_3-L_2 energy shift is 156.7 eV both for the maxima of white lines as well for the XANES structures at higher energy. The half width of the white lines, measured by the analysis of the low energy side, is $\Gamma = 1.2 \pm 0.1$ and 1.4 ± 0.1 eV for the L_3 and L_2 edges respectively. This is in agreement with a full width at half maximum (FWHM) 2 eV determined only by the sum of initial state lifetime (2.1 and 2.5 eV for L_3 and L_2 respectively) and the experimental bandwidth 0.4 eV. Therefore the white line is assigned to a very narrow spike of 4d unoccupied final states and its maximum corresponds to the energy of core excitatons at the Fermi level. The difference between the L_3 and L_2 white lines is due to the predominance of $j=5/2$ total angular momentum of empty 4d holes. Dipole transitions

from the L_2 (j=1/2) core state to the j=5/2 4d holes are forbidden by selection rules $\Delta j=0 \pm 1$ and $\Delta S=0$.
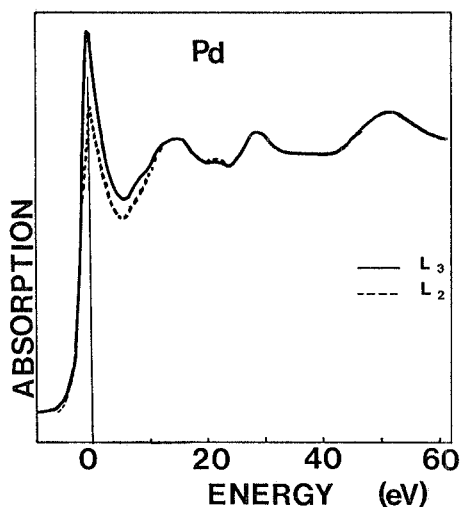

Fig. 1 Pd XANES of L_3 and L_2 . The L_3 edge has been shifted by -156.7 eV.

Fig.2 shows the experimental L_3 XANES compared with the calculated XANES (6). The one-electron local and partial (only the $\ell =2$ component of the partial wave expansion) density of states, calculated by Muller et al., is in very good agreement with the experiment concerning the relative intensity between the white line and the high energy atomic continuum absorption, and the amplitude of XANES at higher energy. The white line is due to an atomic like resonance 2p → 4d and the high energy structures are determined by crystal structure through photoelectron multiple scattering. Only a small cluster around the absorbing atom contributes to the XANES due to lifetime of the excited electron, i.e. to its short inelastic mean free path λ<10 Å at kinetic energies above 10 eV [6-5].
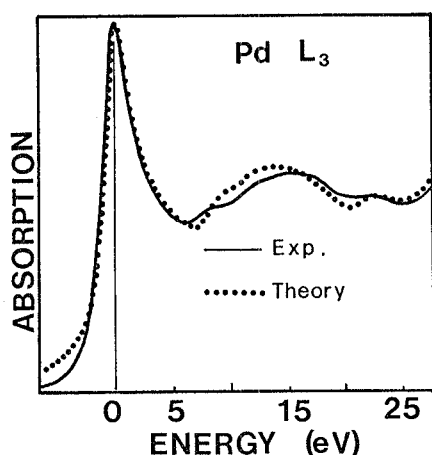

Fig. 2 L_3 high resolution spectrum compared with calculated XANES by Muller et al. (6).

IV.MULTIELECTRON EXCITATIONS IN XANES

Different final state effects are expected in different systems. In the XANES of atom [15] and molecules [16] "shakeup" satellites above the continuum threshold have been clearly identified. In the shakeup a valence electron is excited to unoccupied orbitals because of the sudden creation of the core hole potential, followed by relaxation of passive electrons from ground state orbitals to orbitals of the double ionized atom. "Shakeup" peaks appear above the one-electron threshold and are identified because are not predicted by one-electron XANES theories and leaves a double ionized ion. Recently the presence of a "shakeup" peak has been reported [17] in XANES of insulators by analogy with the "shakeup" peak in the XPS spectra. However, because of the different final states in XPS and XANES, for the presence of the excited extra electron in the XANES final state, the presence of a "shake up" peak in XPS is not enough to predict its presence in the XANES.

In metals we can distinguish different final state regimes from the values of the important interactions which determine the presence of a satellite, its intensity and position [18]: the valence band width (W), the core hole-valence electron coulomb interaction (Q) and the band filling.

For the free electron limit, $Q/W \to 0$, there will be no satellites and the many body effects induce a broadening and asymmetry in the threshold lineshape. This is the well studied Mahan-Nozieres singularity [19] where a continuous spectrum of low energy electron-hole excitations follows the core hole excitation. This effects has a negligible role on the absorption threshold lineshape of transition metals like Pt, Pd and Ni with localized nd band at the Fermi level [10], while it is important in XPS [20].

For the high correlated electron limit $W/Q \to 0$ and partially filled band, the electron hole interaction Q removes the degenerancy between the final state configurations of the many body system, including passive electron. Multiplet splitting appears and interference effects between final state configurations can play an important role [21].

Pd, like Ni and Pt, belongs to the intermediate case Q/W ∿1 with a nearly filled 4d valence band. The Pd ground state configuration $2p^6 4d^{9.64}5sp^{0.36}$ can be described by the overlap of two virtually degenerate atomic configurations: A) $2p^6 4d^9 5sp^1$ and B) $2p^6 4d^{10} 5sp^0$.

Fig.3 shows the evidence of two final state configurations in the 3d core level XPS spectrum measured by Chandesris, Krill et al. [22]. The main line is the "well screened" hole configuration: $3d^9 4d^{10} 5sp$, with an extra 5sp electron screening the core hole. The weak satellite is the "poorly screened" hole configuration: $3d^9 4d^9 5sp^2$ at 6.2 eV higher binding energy, identified as a two hole bound state like the $2p^5 3d^9 4sp^2$ two hole bound state observed in Ni 2p XPS spectrum [23-24].

The intensity of the "two hole satellite" is a measure of the number of nd core holes in the grund state if W/Q ∿ 0; in the intermediate case Q/W ∿ 1 its intensity is still related to the number of nd holes "c", but it is not a measure of the ground state "c" and the satellite peak becomes broader and weaker [25]. The intensity and energy spread of the satellite is expected to be different in the L_2 and L_3 spectra [24].
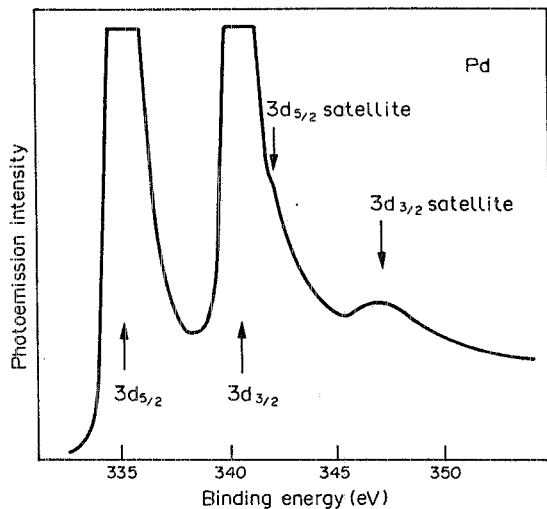
Fig. 3 XPS 3d core line spectrum showing the

   "two hole" satellite at 6.2 eV higher

   binding energy.

In the L_3 XANES the white line is due only to the photoionization of the initial state configuration A. $\hbar\omega +A \rightarrow 2p^5\ 4d^{10}\ 5sp^1$ which corresponds to the "well screened" configuration of XPS (as observed in Ni by Dietz et al. [10]). Because of the filled 4d band no multiplet splitting of final state configurations, inducing a broadening of the white line, can be present. In the case of a photoelectron filling a band Stern and Rehr [26] have remarked that the von Barth and Grossman [7] final state rule can be violated and the local density of states before excitation is appropriate to describe XANES predicting a very good agreement with one particle calculations of the initial states of Muller et al. [6]. Such agreement has been found in our experiment as it is shown in Fig.2.

At photon energies above the white line the well screened hole configuration $2p^5\ 4d^{10}\ 5sp^1\ \varepsilon\ d$ is expected to give the main contribution. This effect can explain the experimental finding of the same energy separations between the white line and the high energy XANES features in the experimental spectrum and in the theoretical initial state density of states shown in Fig.2.

Finally the only energy region where a multi-electron final state feature beyond the one electron description of XANES can appear is at the energy of the two hole resonance $2p^5\ 4d^9\ 5sp^2$ which is expected to form a bound state extending over several eV around 6-8 eV above threshold. The comparison between the experimental and the theoretical one-electron XANES does not show an anomalous structure in this energy range, but the agreement is not so good to exclude a weak broad structure in this energy range. We have compared the L_3 and L_2 spectra in order to see possible anomalies. In Fig.4 we show the difference spectrum between the shifted L_2 spectrum divided by 2.1, to take account of the different statistical weight. With the right chemical $L_2\ L_3$ spin orbit

splitting 156.7 eV all the XANES high energy features disappear in the difference. The negative peak is due to the higher intensity of the L_3 white line and its area gives a measure of the
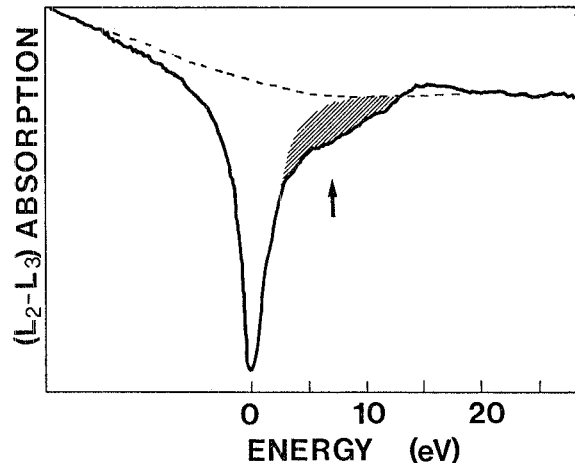

Fig. 4 Difference spectrum of XANES spectra

   $\alpha_{L2}(h - 156.7) - \alpha_{L3}/2.1$. The negative

   peak is due to the higher intensity of

   the L_3 white line. The dashed line is

   the expected background due to high en-

   ergy L_3 EXAFS oscillations at the L_2

   threshold.

number of the j=5/2 4d holes [13,11]. The dashed shoulder, on the high energy side of the negative peak due to L white line, centered at 6 eV and extending up to 13 eV, could be an indication of the presence of a very broad "two hole-two electron" excited state which could be stronger in the L_3 spectrum than in the L_2 spectrum.

An alternative one electron interpretation of the shoulder in Fig.4 is the prevalence of j=5/2 total angular momentum of the electrons of the 5sp band, partially hibridized with the 4d orbitals, on the atomic site because of the exchange interaction with the 4d hole. The dipole selection rule $\Delta S=0$ from the 2p core level to the d component of the 5sp conduction band will give in that case a larger absorption cross section for transitions from the $2p_{3/2}$ level.

In conclusion we have found that all considered many body effects on the L_3 XANES of Pd are negligible in comparison with one electron effects. The only possible indication of a final state effect we have found is in the range from 4 to 13 eV above the Fermi level due to a "two hole and two electron" bound state corresponding to the "two-hole" resonance seen in XPS. However it is so weak that it cannot be seen as a characteristic feature in the XANES but only in the difference spectrum between L_3 and L_2 XANES spectra.

REFERENCES

[1] A.Bianconi, S.Doniach, and D.Lublin, Chem. Phys. Lett. <u>59</u>, 121 (1978) and A.Bianconi, M. dell'Ariccia, P.Durham, and J.B.Pendry, Phys. Rev. B <u>26</u>, 6502 (1982)..

[2] A.Bianconi, Applications of Surf.Sci. <u>6</u>, 392 (1980).

[3] A.Bianconi, Proc. of the meeting "EXAFS for inorganic systems", Daresbury rep. DL/SCI/R17 (1981) p.13 and A.Bianconi et al., J.Mol.Biology (1983), to be published.

[4] F.W.Kutzler, C.R.Natoli, D.K.Misemer, S.Doniach and K.O.Hodgson, J.Chem.Phys. <u>73</u>, 3274 (1980).

[5] P.J.Durham, J.B.Pendry, and C.H.Hodges, Solid State Commun. <u>38</u>, 159 (1981).

[6] J.E.Muller, O.Jepsen, and J.W.Wilkins, Solid State Commun. <u>42</u>, 365 (1982).

[7] U.Von Barth and G.Grossman, Solid State Commun. <u>32</u>, 645 (1979) and Phys. Scripta <u>20</u>, N 39 (1979).

[8] R.D.Leapman, L.A.Grunes and P.L.Fejes, Phys. Rev. B <u>26</u>, 614 (1982).

[9] P.S.P.Wei and F.W.Lyttle, Phys. Rev. B <u>19</u>, 679 (1979).

[10] R.E.Dietz, E.G. Mc Rae and J.H.Weaver, Phys. Rev. B <u>21</u>, 2229 (1980).

[11] M.Brown, R.E.Peierls and E.A.Stern, Phys. Rev. B <u>15</u>, 738 (1977).

[12] A.Bianconi, S.Modesti, M.Campagna, K.Fischer and S.Stizza, J. Phys. C <u>14</u>, 4737 (1981).

[13] L.F.Mattheiss and R.E.Dietz, Phys. Rev. B <u>22</u>, 1663 (1980).

[14] F.W.Lyttle, P.S.P.Wei, R.G.Greegor, G.H.Via, and J.H.Sinfelt, J. Chem. Phys. <u>70</u>, 4849 (1979).

[15] T.A.Carlson, M.O.Krause and W.E.Moddeman, J. Phys. (Paris), Colloq. <u>32</u>, C4-76 (1971) and F.Wuileumier, ibidem C4-88 (1971).

[16] A.Bianconi, H.Petersen, F.C.Brown and R.Z.Bachrach, Phys. Rev. A <u>17</u>, 1907 (1978).

[17] E.A.Stern, Phys.Rev.Lett. <u>49</u>, 1353 (1982).

[18] A.Bianconi, Phys.Rev. B <u>26</u>, 2741 (1982).

[19] G.D.Mahan, Phys. Rev. B <u>14</u>, 3702 (1976).

[20] F.Antonangeli, A.Balzarotti, A.Bianconi, P.Perfetti, P.Ascarelli, and N.Nistico', Solid State Commun. <u>21</u>, 201 (1977).

[21] L.C.Davis and L.A.Feldkamp, Phys.Rev. A <u>17</u>, 2012 (1978) and Solid State Commun. <u>19</u>, 413 (1976).

[22] B.Chandesris, G.Krill, G.Naire, J.Lecante and Y.Petroff, Solid State Commun. <u>37</u>, 187 (1981).

[23] S.Hufner and G.W.Werthein, Phys. Lett. <u>51A</u>, 299 (1975).

[24] A.Bosh, H.Veil, G.A.Sawatzky and N.Martensson, to be published.

[25] L.C.Davis and L.A.Feldkamp, J. Appl. Phys. <u>50</u>, 1944 (1970).

[26] E.A.Stern and J.J. Rehr, to be published.