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**Ni 2p-3d EMISSION SPECTRUM : EXISTENCE OF AN X-RAY RESONANT STATE**

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**RESUME** : Les différences observées entre les spectres d'un nickel massif et d'agrégats de nickel de différentes tailles sont discutées. Un état X résonnant est observé pour les agrégats. On conclut que cet état résonnant 2p existe pour ces systèmes de petite dimension car l'environnement du nickel agit comme une barrière de potentiel confinant les électrons 3d sur les atomes de nickel.

**ABSTRACT** : Differences observed between the spectra of bulk Ni and Ni" clusters of various sizes embedded in an X-zeolite are discussed. An X-ray resonant state is observed for the clusters. It is concluded that this 2p-resonant state exists because nickel has in these small size systems an environment which acts as a potential barrier confining the 3d electrons on the Ni atoms.

**I. INTRODUCTION**

In bulk Ni, the single-excited state having a 2p hole and an electron in the normally empty d states has no quasi-atomic character. This statement is supported by the following facts: 1) the Ni 2p photoabsorption is relatively well described in a band model with the transition probabilities and the 2p hole lifetime effect taken into account [1]; 2) no X-ray resonance line is observed in the bulk Ni 2p emission; these emissions involving the direct radiative recombination of the excited electron to the 2p hole are observable only if the single-excited state is strongly localized [2].

On the other hand, Coulomb correlation effects are expected when a hole is created in any level of a quasi-filled d band. Among the transition metals, nickel is the one for which these correlation effects are expected to be the most noticeable [3]. With the aim of determining the importance of intraatomic interactions on the bulk Ni spectral characteristics, it is interesting to investigate if physico-chemical conditions exist in which the Ni 3d states can have some quasi-atomic behaviour. Thus we have analyzed the densities of states of small particles. In fact, atomic characteristics are expected to appear as the size decreases.

We report here our results on the X-ray spectral densities of embedded Ni small particles. We discuss the changes observed with the size relative to the bulk. Informations on the importance of interactions of interatomic and intraatomic type are deduced for the analyzed particles and consequently for the bulk.

**II. EXPERIMENTAL RESULTS**

The samples used were Ni_{10}Ca_{20}Na_{4}H_{19} X zeolite treated...

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in order to obtain an almost homogeneous dispersion of Ni° clusters located in sodalites or in supercages. Details of preparation and characterisation are described elsewhere [4]. Let us recall that from FMR experiments these clusters are superparamagnetic. Static magnetism shows that the mean diameter of the Ni° clusters in sodalite is less than 0.65 nm (corresponding to clusters of about 8 atoms) and 1 nm (about 50 atoms) in supercages. A mono granular layer of the zeolite is stuck onto a cooled copper target.

Spectra are performed in a 500 mm radius bent crystal vacuum spectrometer. A (1010) beryl crystal is used in the first order of reflection. The detector is a Ar-CH₄ flow gas counter. The energy of primary electrons is chosen in order 4 to minimize satellite emission and self absorption in the target. In the spectral range studied (845-860 eV), the resolving power is about 1750 [5], mainly as a result of the angular width of the reflection curve of the beryl crystal. Nevertheless, the experimental accuracy is better than 0.1 eV for the measurement of energies. The spectra of clusters are compared to that of bulk nickel obtained under the same experimental conditions.

The Ni 2p³/₂ - 3d emissions of 50 atoms and 8 atoms clusters are shown fig. 1-a, 3/2 and 2-a respectively. The maximum (labelled $\Delta$) of the emission coincides (± 0.08 eV) with that of bulk nickel (curve 1-a'). The main characteristic of the clusters spectra is the appearance of fine structure [6][7] which is more marked for the 50 atoms spectrum than for that of the 8 atoms. For a better characterization of the clusters spectra, we show the difference curves between the spectra of the clusters and of the bulk nickel in each case (fig. 1b,2b).

Towards lower spectral energies, the 50 atom cluster emission is slightly narrowed as clearly seen by negative values on the spectra difference for energies lower than $E_X$. In contrast for the 8 atoms clusters, no contraction is observed but positive and negative
values on the spectra difference on each side of $E_g$ denote a clear change in the shape of the cluster emission.

On the high energy side, both spectra show a structure labelled $E$ in the range around 853 eV, i.e. in the 2p$_{3/2}$ photoabsorption range of bulk nickel. However for the 50 atoms clusters, the structure $E$ appears as a strong contribution of positive values which coincides with the peak A of Ni 2p$_{3/2}$ photoabsorption while for 8 atoms clusters the contribution corresponding to $E$ is weaker and appears shifted towards higher energies by about 0.5 eV. The structure $E$ evidences the existence of an X-ray resonant emission in these systems.

**DISCUSSION**

For bulk Ni, the d occupied spectral densities as seen by XES and XPS are known to be narrower than the theoretical d DOS calculated for the metal in the ground state. In both experiments, the spectral densities describe a hole in the valence band weighted by transition probabilities. They retain the character of a continuous band and no feature is seen in the X-ray 2p-3d emission (cf. figures).

The X-ray high-energy satellite of bulk Ni can be due to the creation of doubly-excited or ionized states with 2p$_{3/2}$ and 3d holes by shake-up effect followed by a radiative recombination to a final state with two 3d holes. On the other hand, when the energy $E_o$ of incident ionizing particles is higher than the 2p$_{3/2}$ threshold, the intermediate state with 2p$_{3/2}$ and 3d holes can be created by 2p$_{3/2}$-2p$_{3/2}$ 3d Coster-Kronig transition; this state decays to the same final state with two 3d holes making the shake-up and Coster-Kronig satellites indistinguishable. As already underlined [8], the satellite is a continuous emission band and no feature characteristic of transitions from a quasi-atomic state with two 3d holes is seen in the bulk Ni X-ray spectrum whatever the value of $E_o$ (figure 1). The Auger transitions having the same final state show an analogous behaviour. [9]

In contrast, in the cluster spectra, structures are observed which vary according to the size.

For both clusters, a resonant emission ($E$) is observed. Such a radiative process is present only if the lifetime of the excited state is of the same order as the core hole lifetime (here $9.10^{-16}$s since the Ni 2p$_{3/2}$ level is 0.7 eV wide). This emission characterizes the localisation due to the size effect that suffers an electron excited in the empty d densities in the presence of the core-hole.

For the 50 atom clusters, the resonant emission coincides exactly with the bulk photoabsorption peak. Moreover no 3d transition characteristic of a Ni 3d-ligand orbital mixing is observed. This suggests that the Ni cluster-zeolite interaction is weak. The contraction of the emission spectrum can then be related to the decrease in the mean coordination number in agreement with calculations and photoemission results. In this model, there are the Ni-Ni interactions which essentially govern the distribution of Ni 3d filled states. Then the emission structures, others than $E$, can be interpreted by a partial removing of filled 3d states degeneracy due to the size effect. On the other hand, the walls of the supercage form a repulsive potential barrier which confines the 3d electrons in the cluster leading to a localisation of 3d states. This localisation favours the degeneracy removing of 3d filled orbitals and stabilizes the excited state precursor of the resonant emission.
In the 8 atoms clusters, all the atoms are surface ones and each Ni has only four Ni next neighbours. Consequently the interactions between nickel and zeolite, mainly oxygen of the sodalite walls, must be taken into account. Indeed the relatively large and little structured line observed for this system can be explained by interactions between the Ni d states and the densities of states of the solid zeolite. However the emission is different from that of NiO: no crystal field splitting of the 3d states is observed. On the other hand, the higher energy feature, $\varepsilon$, is shifted in the direction of the Ni photoabsorption peak in NiO in spite of the fact that no such feature is seen in the 3d emission of NiO. Then the spectrum is characteristic of Ni clusters in which all the atoms have oxygen neighbours at distances clearly larger than in the defined compound. In such a system, the spectral density is not dominated by the Ni-Ni interactions but by the interactions between the Ni 3d states and the walls of the cage as revealed by the spectral characteristics: broadening of the 3d filled state distribution and shift of the resonant emission.

CONCLUSION

The structures observed in the X-ray emission band for embedded Ni clusters depend strongly on the environment. This shows that interactions of the interatomic type play a predominant role on the shape of spectral densities for such systems. In particular the characteristics of the X-ray resonant state varies with the environment proving that this state is due to the potential barrier induced by the conjugate effect of the particle size and the cage walls.

Conversely, the intraatomic correlations do not dominate and only partial atomic character is present in the X-ray spectral densities of the embedded particles. Then a purely atomic model cannot be used to describe them. A fortiori, such a model is not valid to describe the bulk Ni spectra, as already expected from the absence of atomic character in the X-ray and Auger spectra of this metal.

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