STUDY OF Mo–Ni ALLOYS
BY X-RAY SPECTROSCOPIES

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Dedicated to Professor Dr. Julian Auleytner
on the occasion of his 70th birthday

Band structure investigations of the random $MoNi_4$ and $MoNi_3$ alloys, performed by emission and photoelectron spectroscopy, is reported. The X-ray emission and X-ray photoelectron spectra allowed to study the occupied valence band states below Fermi level. These techniques gave the full description of changes in the density of valence electron states distribution due to substitution of Mo atoms into the fcc Ni lattice up to 25 at%. The analysis of the emission and photoelectron spectra led to clear distinction between the changes in spectra caused by density of states structure and by additional effects involved in creation of the particular spectra. The experimental data are compared with the density of states calculated using coherent potential approximation and linear muffin-tin orbital methods.
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1. Introduction

During the last two decades a considerable progress has been done in the studies of electronic structure by X-ray and electron spectroscopies. There exist several techniques which can be used to study the valence band structure of materials. In the present paper the X-ray emission spectra (XES) and the X-ray photoelectron spectra (XPS) were applied to attain the full picture of the distribution of

valence band density of states (VB DOS) in the random $MoNi_4$ and $MoNi_3$ alloys. The particular advantage of the emission spectroscopy in alloys and compounds is that this technique projects the DOS at the site of the emitting atom. This enables to test the calculations of partial DOS for each component. Furthermore, XES are especially suitable for studies of the electronic structure of bulk materials because of the deep penetration of the X-ray signal. The X-ray photoelectron spectra are used to study the DOS distribution summarized for both atoms. This technique is surface sensitive. The depth of penetration of the signal is in the order of 15–20 Å for Mo–Ni alloys. Therefore, special attention should be paid to the problem of removing the surface contamination without affecting the composition [1, 2]. The DOS distributions for alloys were calculated using the coherent potential approximation (CPA) and linear muffin-tin orbital (LMTO) method. The dependence of the spectra on the alloy composition as well as the influence of the alloy disorder on DOS and spectra shape were discussed.

2. Experimental procedure

The polycrystalline Mo–Ni samples were prepared from the high purity rod of Mo and Ni by repeated arc melting of weighted amounts of both materials in a helium atmosphere. An X-ray microprobe was used to check the chemical composition at several different places of samples surface. The composition of alloys was homogeneous within 2%. The samples were cut into 1 mm thick slices. To form the disordered fcc structure the alloys were annealed for two hours in vacuum (10^{-4} Pa) at temperature 1373 K and next quenched to room temperature. The structure was checked by X-ray diffraction. The samples were mechanically polished using an emcry paper and ultrasonically washed in the acetone bath just before the measurement of spectra.

The L_α X-ray emission spectra (XES) of Ni were recorded by the X-ray fluorescence single-crystal spectrometer (SARF1) [3]. The copper anode (supplied with 7 kV voltage and 0.8 A current) produced the radiation to excite the L_α emission spectra of Ni. The KAP crystal was used to analyze the radiation. The vacuum in the spectrometer was in the order of 10^{-4} Pa. The geometrical resolution was 0.5 eV. A gas flow proportional counter was used as a detector.

The M XES of Mo were recorded by the soft X-ray grating spectrometer (RSM-500) [3]. The electron beam (3 kV, 10 mA) was used to excite the spectra. The vacuum in the X-ray tube was 10^{-4} Pa. The samples were cleaned from surface contaminants by Ar^+ ion bombardment. The thickness of altered layer where the composition changes after the ion sputtering is of the order of 10–25 Å and in comparison with the depth of X-ray signal penetration (4 μm) can be neglected. The K_α lines of carbon and oxygen were monitored before recording the Mo spectra. It appeared that the samples were oxygen-free with only a small amount of carbon contaminant. The M_ξ and $M_{IV,V}$ spectra of Mo for elemental Mo and alloys were recorded. The geometrical resolution was 0.7 eV. The photoelectron multiplier with CsJ photocathode was used as an X-ray detector.

The XPS were measured by VG ESCA3 instrument using a monochromatized Al K_α X-ray source. A base pressure in the chamber was 10^{-7} Pa. The energy resolution was 0.6 eV as estimated from the FWHM of the Cu $2p$ line. The valence band spectra of pure Ni, Mo and their alloys were recorded after removing the surface contaminants by scribing *in situ*.

3. DOS calculation

Considering the random face centered cubic structure (fcc) of MoNi$_4$ and MoNi$_3$ alloys we assumed two limiting cases: (i) no preference in the Mo and Ni atoms position in the unit cell and (ii) the AuCu$_3$ (L1) type of the fcc unit cell for the MoNi$_3$. The coherent potential approximation (CPA) [4] was used in calculation of d-local DOS (LDOS) and total DOS (TDOS) in the first case. The way to obtain reasonable solutions for Hamiltonians having random potentials has a long and complex history [5]. A paper by Velicky et al. was of particular importance [6], which clarified the standing of the CPA as being the best possible approximation within so-called single-site approximation. The main idea of this approximation lies in defining some effectively ordered system with the corresponding effective potential function which can be placed on every site in the alloy and used to resolve the Schrödinger equation. The best choice for unknown effective coherent potential is then obtained by satisfying some constraints. This model was applied for the calculations of electronic structure of MoNi$_3$ and MoNi$_4$ random alloys. The DOS of pure nickel was used as the base. Calculations were performed for three different values of the dimensionless parameter w_B characterizing the transfer integrals between the atomic sites (proportional to $dd\sigma(\text{Mo–Mo})/dd\sigma(\text{Ni–Ni})$) [6]. According to the analysis performed in paper [7] the value $w_B = 4.72$ gave the best agreement with experiment. The TDOS and LDOS for this value of parameter are presented in Fig. 1. The separation between the atomic levels was determined to satisfy the charge neutrality condition on each atomic site. In order to determine the Fermi energy we assumed the number of d electrons of Ni and Mo atoms to be 9.08 and 5.07 per atom, respectively [6]. To estimate the influence of disorder effect on DOS calculations and on spectral features the linear muffin-tin orbital (LMTO) method [8] was used to calculate the electronic band structure for the MoNi$_3$ alloy under assumption of L1 structure. The exchange and correlation interactions were treated within local density approximation using Barth–Hedin parametrization. The relativistic effects, except spin–orbit coupling, were included in the calculation. The outermost s, p, d and f electrons were treated as the valence states, while the charge density of the remaining electrons was kept fixed (the frozen-core approximation). In the self-consistent procedure, the diagonalization of the LMTO Hamiltonian was performed at 35 k points in an irreducible part of the Brillouin zone. The LDOS (Mo $p+f$ and Ni $s+d$) and TDOS for L1 structure calculated in the tetrahedron method [9] are shown in Fig. 2.

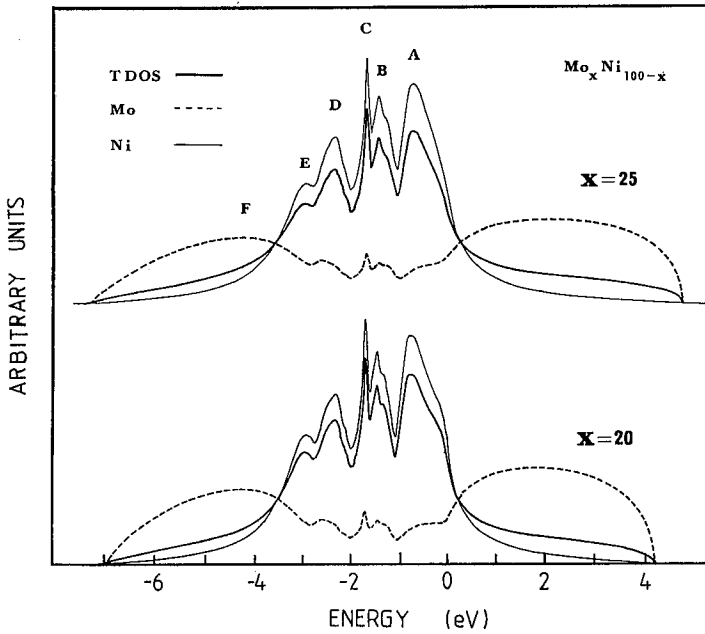Fig. 1.   The LDOS and TDOS for the random MoNi$_4$ and MoNi$_3$ alloys calculated by the CPA method.
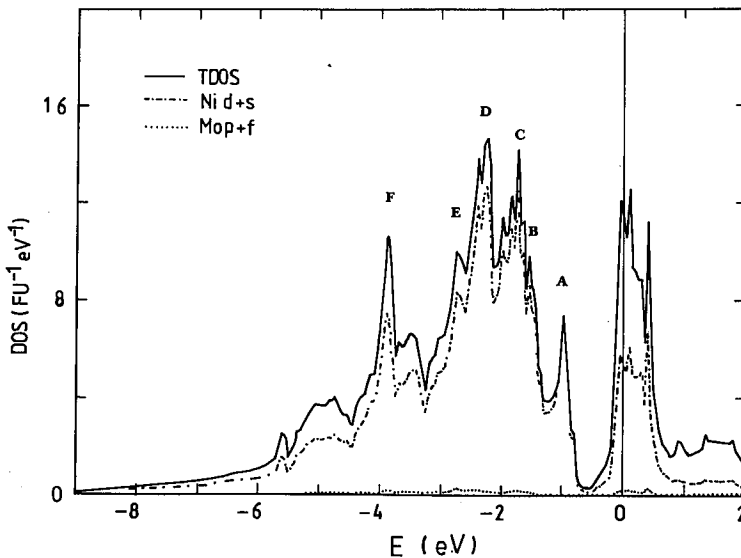

Fig. 2.   The LDOS (Mo $p + f$ and Ni $s + d$) and TDOS for the L1 structure of MoNi$_3$ alloy calculated by the LMTO method.

4. Result and discussion

The L_α XES of pure Ni and Ni in alloys are presented in Fig. 3. The intensity of the spectra was normalized to the same value at maximum. The position of zero energy was chosen in such a way that the position of maximum intensity agreed with the appropriate maximum of DOS. The transition of d and s symmetry valence electrons to the hole at $2p_{3/2}$ level created the L_α emission spectrum. The L_α spectrum for pure Ni is in good agreement with the spectra reported in literature, e.g. [10, 11]. The several physical processes involved in the creation of L_α spectra disturbed the picture of d-like states distribution: (i) natural width of the core level (the width of the $2p_{3/2}$ level in Ni is 0.7 eV [10]), (ii) the final state effects, (iii) the self-absorption and (iv) the two-vacancy satellite. The influence of all these effects on the shape of Ni L_α line in the considered alloys was discussed previously [3]. Thus, in the present paper we restrict discussion only to the changes of spectra due to alloy, in reference to the elemental Ni spectrum. The disordered $MoNi_4$ and $MoNi_3$ alloys have the same structure as elemental Ni (fcc). The number of Ni nearest neighbors for Ni atoms changes with composition of alloys. The spectra do not show any fine structure. A small shift of the maximum towards the Fermi level (0.2 eV) and an increase in FWHM were observed as compared with pure Ni (Table I). The most pronounced changes of spectra width appear on the high-energy side of the peak. The spectra become more symmetric (see asymmetry parameters given in Table I) and the density at the Fermi level increases. These changes should be associated primarily with a decrease in self-absorption related
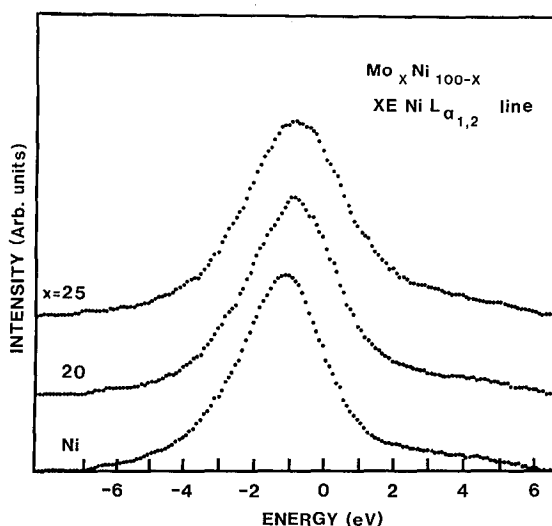

Fig. 3. The L_α X-ray emission spectra of the pure Ni and Ni in alloys. The intensity was normalized to the same value at the maximum. The zero at the energy scale was chosen in such a way that the position of the maximum intensity of spectra agrees with the corresponding maximum of DOS.

The characteristic features of L_α and $M_{IV,V}$ spectra.

Composition in at% Mo	FWHM [eV]	Asymmetry parameter	Maximum position [eV]	Band bottom width [eV]	Band area [arb. unit]	Intensity at Fermi level [arb. unit]
L_α 0	2.8	1.30	−0.9	5.5	−	53
20	3.1	1.00	−0.7	6.1	−	62
25	3.3	0.90	−0.7	6.6	−	66
$M_{IV,V}$ 0	4.4	−	−1.7	7.7	460	29
20	5.2	−	−1.5	10.3	450	39
25	5.3	−	−1.7	10.3	460	34
error	±0.2	−	±0.2	±0.2	±50	±7

to a decrease in Ni content. Furthermore, the comparison of CPA DOS for $MoNi_4$ and $MoNi_3$ alloys shows only the 0.5 eV increase in the band bottom width in alloys with the decrease in Ni content and this increase is observed also in spectra.

The $M_{IV,V}$ spectra for Mo and alloys are presented in Fig. 4. The intensity was normalized with respect to the intensity of the M_ξ line. The recorded $M_{IV,V}$ spectrum for elemental Mo is in good agreement with the spectra reported previously [12, 13]. The detailed discussion of the elemental Mo spectrum and comparison with the theoretical data was presented in paper [3]. A transition of an electron from the p and f symmetry states of the VB to the $3d_{5/2}$ level hole creates the M_V emission spectrum. The natural width of the $3d_{5/2}$ level is equal to 0.7 eV [12]. The shape of the spectrum of alloys changes as compared with the spectrum of pure Mo. The FWHM of spectra of the alloys increases considerably. The position of the first maximum A changes only within the error limit, but the position of the second maximum B is shifted in the direction of low energy and is marked by D. The intensity at maximum D is lower than at maximum B and the position of band bottom is shifted by about 1.7 eV in comparison with the corresponding position for elemental Mo. The intensity at the Fermi level for the 20 at% of Mo increases and this change is out of the experimental error. On the other hand, the transition to the M_{IV} ($3d_{3/2}$) and self-absorption disturb the high-energy edge of the spectra and an exact estimation from XES of the intensity at the Fermi level is impossible. The distance between the M_ξ and $M_{IV,V}$ line does not change in alloys. This is in agreement with the photoelectron measurements. After normalizing the intensity to the same value of the M_ξ line intensity, the area of the recorded peaks does not change. Therefore, there is no evidence for a charge transfer between different metal atoms. Only the noticeable redistribution in shape of Mo valence band is observed when the atoms are located in alloys in the fcc structure. The number of electrons near the Mo atom is still the same. The
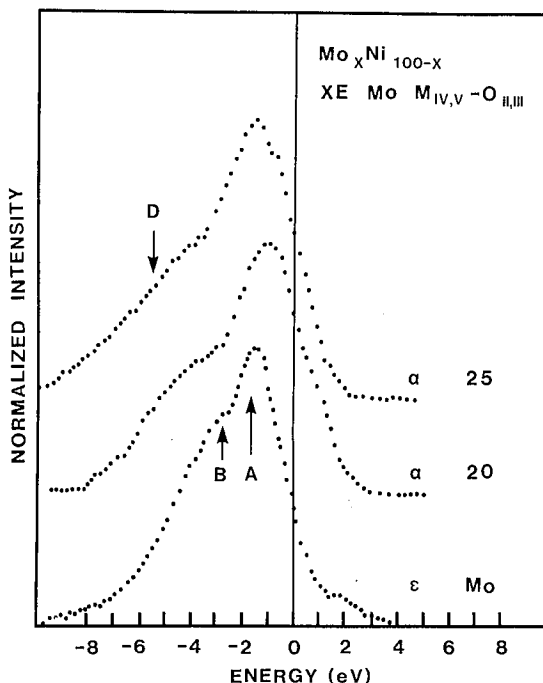
Fig. 4. The $M_{\text{IV,V}}$ X-ray emission spectra of the pure Mo and the Mo in alloys. The intensity was normalized with respect to the intensity of M_ξ line. The zero at the energy scale was chosen as in Fig. 3.

intensity of M_{IV} satellite is much lower for alloys despite reduced self-absorption. The increase in the width of Mo band bottom in alloys with the decrease in the content of Ni is predicted by CPA calculations and was observed in the spectra. However, only the d-like states of Mo can be calculated by the CPA. To calculate the $p + f$ states the LMTO method under assumption of L1 order in MoNi$_3$ alloy was used. The DOS distributions obtained by LMTO and CPA methods for MoNi$_3$ show the same positions of peaks but different intensities (Fig. 2). In order to compare the calculated LDOS with the measured spectra the appropriate LDOS were convoluted with Gaussian broadening functions, to account for the spectrometer resolution and Lorentzian functions to account for the core level width. The results of calculations are presented in Fig. 5. The Ni L_α spectrum calculated from CPA is too broad whereas the L_α and M_V spectra resulting from LMTO calculations are too narrow as compared with the experimental spectra. Disorder causes smoothing of the fine structure, change in the relative intensities of peaks and broadening of the DOS distribution.

The VB XPS for Ni, Mo and alloys are presented in Fig. 6. The total DOS from Ni and Mo atoms are projected in XPS VB of alloys. Characteristic features of the spectra are listed in Table II. The exact comparison of the pure Mo and Ni spectra with the theoretical DOS were presented in our earlier paper [1]. The
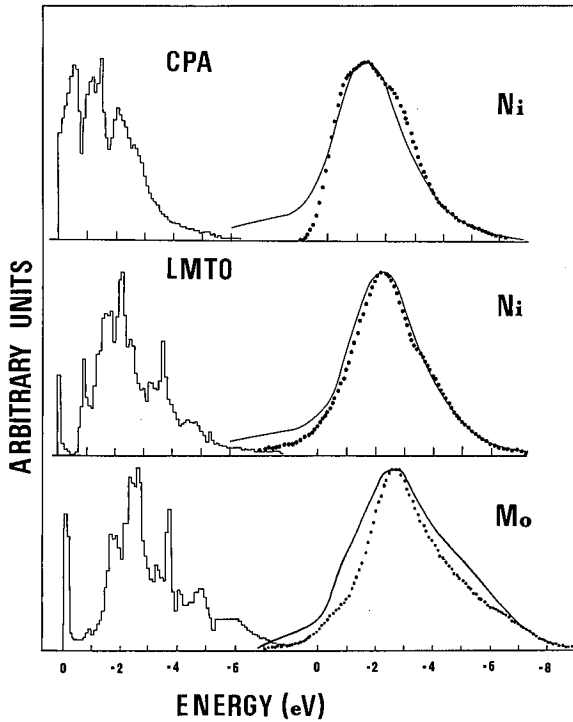
Fig. 5.   The L_α spectra of Ni and the M_V spectrum of Mo for MoNi$_3$ calculated from appropriate DOS (dotted line) and the experimental spectra (full line).

TABLE II

The comparison of characteristic features of XPS and calculated total DOS.

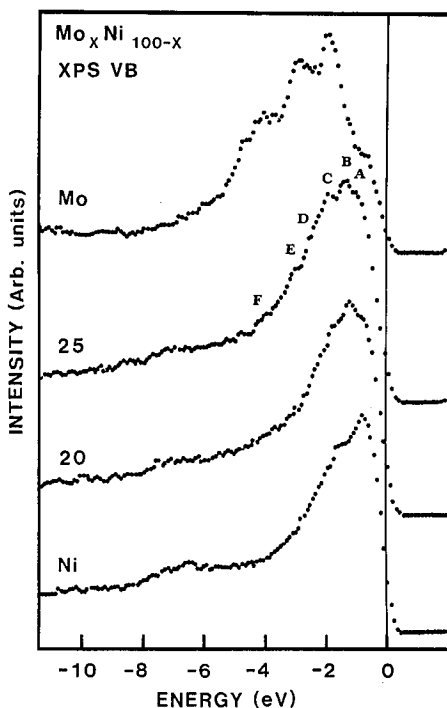| Character. feature position	MoNi$_3$ XPS [eV]	MoNi$_3$ DOS (CPA) [eV]	MoNi$_3$ DOS (LMTO) [eV]	MoNi$_4$ XPS [eV]	MoNi$_4$ DOS (CPA) [eV]
A	−0.8	−0.8	−1.0	−0.8	−0.8
B	−1.3	−1.4	−1.5	−1.2	−1.5
C	−2.0	−1.8	−1.7	−1.8	−1.8
D	−	−2.3	−2.3	−2.2	−2.4
E	−3.0	−3.0	−2.8	−	−3.0
F	−4.0	−3.8	−3.8	−	−4.0
error	±0.2	±0.1	±0.1	±0.2	±0.1

Fig. 6.   The XPS valence band spectra of the pure Mo and Ni, MoNi$_4$, MoNi$_3$ alloys measured for clean surface obtained by scribing *in situ*.

fine structure of the VB spectra changes considerably after addition of Mo. The additional maximum B shifted by about 0.5 eV in the direction of lower energy appears. The third maximum C is located at −1.8 and −2.0 eV for the 20 and 25 at% of Mo respectively. The increase in intensity at low-energy edge of spectra was also observed. Extra VB states arising from Mo atoms are responsible for these changes (see the local DOS calculations shown in Figs. 1 and 2). The main maximum of Mo VB does not shift in alloys but the new, low-energy structure appears as can be seen in the $M_{\mathrm{IV,V}}$ spectra. The two-vacancy satellite at 6 eV is not so well visible as in the XPS VB of the pure Ni. The increase in intensity at the Fermi level was observed in XES at the site of Mo and Ni atoms but there was no evidence of such changes in the XPS VB spectra and in the calculated DOS. Thus, one can conclude that this effect is due to the changes in self-absorption in the Ni and Mo XES. The width of XP and XE VB spectra is larger in alloys than in elemental metals. This indicates that the d-like states are not so well localized in alloys as in pure metals.

5. Conclusion

The results of present investigation can be summarized as follows:

1) The d-like states of Ni in the MoNi$_4$ and MoNi$_3$ alloys are not so well localized as in the pure Ni. The FWHM and width at the bottom of L_α spectra

increase with the decrease in Ni nearest neighbor in the vicinity of emitting atom. This conclusion is consistent with the CPA and LMTO calculations.

2) There is no evidence of charge transfer between different metal atoms. The noticeable redistribution in the Mo valence band is observed when the atoms are located in the fcc structure of alloys.

3) The DOS resulting from CPA and LMTO calculations shows peaks at the same energetic positions (Table II) but the relative intensities of peaks are different.

4) The disorder, characteristic of random alloys, causes the redistribution of the intensity and additional broadening of the DOS structure. The spectra resulting from the LMTO calculations (under the assumption of L1 ordering) are more narrow than the experimental spectra. On the other hand, the spectra resulting from CPA (under an assumption of the full disorder) are broader than experimental spectra.

5) The characteristic features of calculated DOS can be distinguished in the XP VB spectra.

6) The satellites, well visible at L_α, M_V and XP VB spectra of pure metals are much less pronounced in the spectra of alloys.

7) The analysis of the results obtained by the XES and XPS studies allows us to distinguish between the changes in spectra caused either by the changes in DOS structure or by an influence of additional effects involved in the creation of particular spectra.

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