

LNF-90/111

K. Lawniczak-Jablonska, S. Mobilio, J. Inoue, K. Tohyama

**INFLUENCE OF ORDER-DISORDER TRANSITION ON VALENCE BAND
STRUCTURE IN MoNi₃ ALLOYS**

Estratto da: Conf. Proc. Vol. 25 XSR-89, A. Balerna, E. Bernieri, S. Mobilio (Eds.)
SIF Bologna, Pag. 701 (1990)

INFLUENCE OF ORDER-DISORDER TRANSITION ON VALENCE BAND STRUCTURE IN MoNi_3 ALLOYS

K. Lawniczak-Jablonska

Institute of Physics, Polish Academy of Sciences,
Al. Lotnikow 32/46, PL-02668 WARSAW, POLAND

S. Mobilio

INFN Laboratori Nazionali di Frascati, CP-13,
I-00044 FRASCATI (Rome), ITALY

J. Inoue and K. Tohyama

Department Applied Physics, Nagoya University,
464-01 NAGOYA, JAPAN

The change of the number of nearest-neighbours and variation of distance to a given atom in unit cell of binary alloy should disturb the distribution of valence electrons. In the present work this problem is considered theoretically and experimentally for MoNi_3 alloy.

The densities of states (DOS) were calculated for the three model cases: i) no preference at the position of Mo and Ni atoms in fcc unit cell, disordered alloy; ii) the AuCu_3 type of fcc unit cell, short-range order (SRO) alloy; iii) the orthorhombic type of unit cell, long-range order (LRO) alloy. The d-local DOS (LDOS) and total DOS (TDOS) were calculated by several theoretical approaches. The coherent potential approximation (CPA) were used for disordered alloy [1]. The tight-binding d-band model [2] was adopted for fcc and orthorhombic type of unit cell (fig.1).

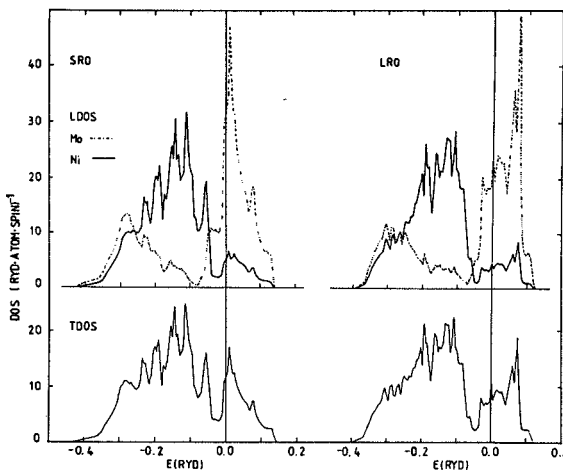


Fig.1
The d-local and total
DOS calculated by
making use of the
tight-binding (TB) d-
band model for fcc
 AuCu_3 (SRO) and
orthorhombic (LRO)
type of unit cell.

The linear muffin-tin orbitals (LMTO) method [3,4] was used to calculate the s+d-like Ni and p+f-like Mo DOS in fcc AuCu₃ type unit cell. The DOS were calculated for occupied the part of the valence band and 2 eV above the Fermi level. For this reason we have compared the X-ray emission spectra with the results of calculation, but we discuss only the edge near Fermi level in absorption and isochromats spectra. Electron distributions at the site of Ni atom were estimated from X-ray L_α emission and X-ray K absorption spectra. The Ni X-ray L_α emission spectra were calculated within simple one electron model to compare the prediction of the theory with experimental results. The d-like LDOS of Ni were convoluted with two broadening functions. The lifetime width of the 2p_{3/2} core level was estimated to be a Lorentzian function with full width at half maximum intensity (FWHM) equal to natural width of 2p_{3/2} level in Ni (0.8 eV). The instrumental broadening was approximated by Gaussian function with 0.5 eV FWHM. The results are presented in fig.2. Best agreement with experimental spectrum has been found for LDOS resulting from LMTO method. Calculations made under assumption of no preference in the position of Mo and Ni atoms (CPA) overestimated the intensity at the peak of experimental spectra. We concluded that even in the so called disordered alloy some short-range order in position of atoms exists. The valence electrons distribution is influenced mostly by atoms in first coordination sphere.

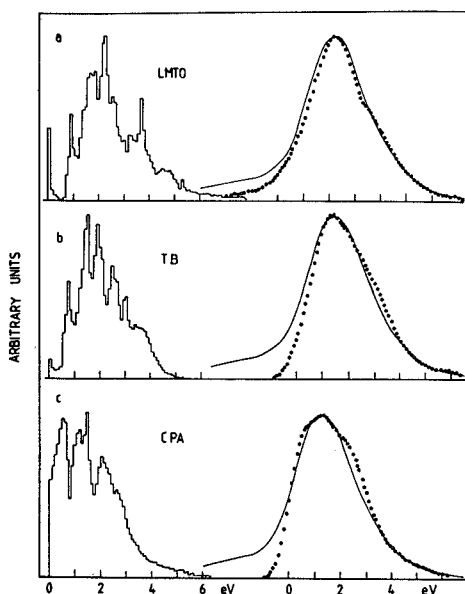


Fig.2.
a) The d+s-like LDOS of Ni calculated by LMTO method and LDOS convoluted with broadening functions (dotted line), experimental L_α emission spectrum for fcc structure MoNi₃ sample (full line).
b) The d-like LDOS of Ni calculated by TB method and LDOS convoluted and compared with experimental spectrum like in a).
c) The d-like LDOS of Ni calculated by CPA method and LDOS convoluted and compared with experimental spectrum like in a).

Comparison of the calculated spectra with the experimental spectra for fcc AuCu₃ and orthorhombic types of unit cell is presented in fig.3. The orthorhombic LRO structure was formed after four days annealing at the temperature of 1013K. Direct comparison of d-like LDOS (fig. 3a) shows

that the DOS at the peak is wider and the edge near Fermi level is sharper for orthorhombic structure than for AuCu_3 . The same differences result from comparison of the calculated spectra (fig.3b) and experimental spectra (fig.3c). Thus, the change in atomic order around Ni atoms leads to the redistribution of valence electrons near the Fermi level and change the shape of Ni L_α spectrum. Both experimental spectra near the Fermi level edge are influenced by the two-vacancy satellite and by self-absorption effects.

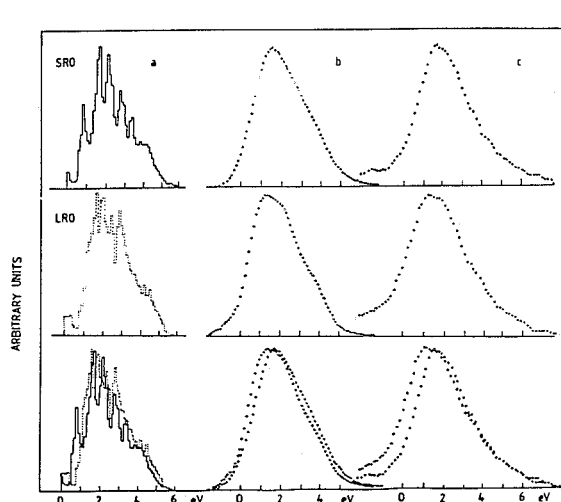


Fig.3.
a) The Ni d-local DOS for SRO and LRO and comparison of both DOS.
b) The Ni d-LDOS after convolutions with broadening functions for SRO and LRO and comparison of both calculated spectra.
c) The experimental Ni L_α spectra for SRO and LRO sample and comparison of both spectra.

The Ni K-edge absorption spectra for elemental Ni and MoNi_3 fcc alloy are presented in fig.4. Presence of Mo atoms in neighborhood of Ni atoms changed the characteristics of the Ni DOS structure. The increase of the intensity in maximum A and the suppression of intensity in maxima C, D and E is accompanied by the shift of the maxima position in the high energy direction.

The empty states of both Ni and Mo are projected in bremsstrahlung isochromat spectra (BIS). The spectra of BIS are presented in fig.5. In creation of BIS the electron transition between two states above the Fermi level are involved. This process is not influenced by inner core levels. The addition of Mo atoms change the shape of Ni BIS. The Mo have the high DOS near Fermi level and the intensity of Mo bremsstrahlung radiation is higher than for Ni (Z^2). Considerable increase of the intensity at the first maximum was observed. The detail comparison of this maximum for fcc and orthorhombic alloy showed, that the near Fermi level edge is sharper and valley after first maximum is lower for fcc structure alloy. This agree with calculated DOS distribution above Fermi level. The second maximum is sharper and more narrow than second maximum for orthorhombic structure.

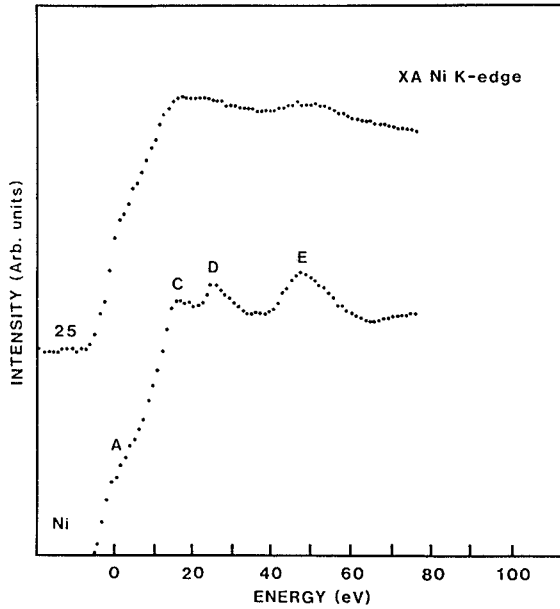


Fig.4.
The Ni K-edge
absorption spectra
for Ni and MoNi₃
disordered fcc alloy.

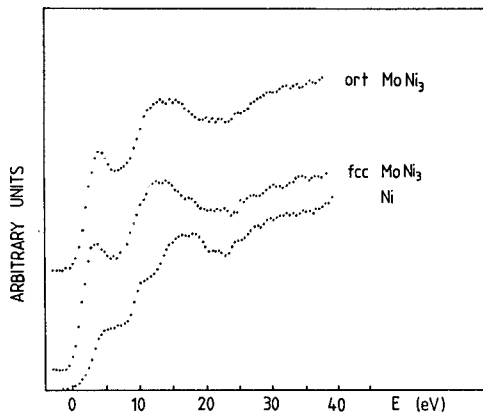


Fig.5.
The bremsstrahlung isochromat
spectra at the phonon energy
5414 eV for elemental Ni, for
fcc disordered, and for the
LRO MoNi₃ sample.

In summary we conclude that the change of atomic order between fcc and orthorhombic structures in MoNi₃ alloy cause the redistribution of valence electrons in occupied and unoccupied part of valence band. These changes are predicted by the theoretical models.

References

1. P.A. Papaconstantopoulous, Handbook of Band Structure of Elemental Solids, Plenum Press, New York, 1986
2. M. Shimizu, J. Inoue and S. Nagasawa, J. Phys. F: Met. Phys. 14 (1984) 2673
3. O.K. Andersen, Phys.Rev. B12 (1975) 3060
4. J. Inoue, K. Tohyama, to be published