STUDY OF CHANGES IN L\(_{3,2}\) EELS IONISATION EDGES UPON FORMATION OF Ni-BASED INTERMETALLIC COMPOUNDS

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Changes in the experimental EELS L\(_{3,2}\) edges of transition metals upon the formation of NiMn and TiNi and NiAl 50:50 intermetallics are investigated and related to the redistributions of the density of state (DOS) in the valence d-bands\(^1\). These edges appear due to the transitions of excited inner p\(_{1/2}\) (L\(_2\) edge) and p\(_{3/2}\) (L\(_3\) edge) electrons to nearest empty electronic states in the valence band. The dipole selection rule allows the transition into the d- or s- final states only, and as the probability of a transition to s-states is much smaller than that to d-ones, only the d valence band needs to be considered. Thus, the study of the integral EELS cross section at L\(_{3,2}\) edges yields information on the total d-charge around a given element whereas the details of the electron-loss-near-edge-structure (ELNES) relate to the actual d-DOS distribution above the Fermi level (E\(_F\)).

Fig.1a shows the fine ELNES details of the experimental Ni L\(_3\) edges in pure metal and in intermetallic compounds. The edges were background subtracted, deconvoluted from the plural scattering and scaled following the procedure by Pearson et al.\(^2\) As has been reported previously\(^3\),\(^4\), the NiAl intermetallic compound shows a splitting of the major peak in two subpeaks of reduced height. The difference among other intermetallics is much less and can be described as follows: i) the major peak is narrow in Ni and NiMn but wide in TiNi, ii) the small secondary peak locates around 8eV after the threshold in pure Ni and NiMn but it is shifted to higher energies in TiNi.

These features are well reproduced by ab-initio calculations with a FLAPW method in its WIEN97 implementation. In NiAl, the calculated EELS profile shows the pronounced peak splitting, which is caused by hybridisation between the Al sp- and Ni d-states\(^3\),\(^4\). In TiNi, calculations indeed predict the widening of the major peak and the shift of the secondary one, although the latter is slightly overestimated compared with the experiment. The analysis of the d-partial DOS shows that these effects appear due to the energy resonance between d-Ni and d-Ti states. To illustrate this point, the calculated unoccupied Ni d-DOS is plotted in Fig. 2 in comparison with the corresponding Ti d-DOS. In TiNi, the Ni d states are peaked at the same energy positions as the Ti d states over a large energy region from E\(_F\) to E\(_F\)+10eV. In analogy with a sp-d hybridisation, this effect could be interpreted as a hybridisation between the d-Ni and d-Ti states. However, the charge transfer between Ni and Ti atoms measured from the integral EELS cross sections appears to be less than 0.1 e/atom. Thus, a hybridisation does not imply the spatial mixing of the electrons belonging to different atoms but rather indicates the correlation in the energy levels of Ni and Ti d states.
Fig. 1 Experimental (a) and calculated (b) fine ELNES of the Ni L$_3$ edge in pure Ni and different intermetallic compounds.

Fig 2 Calculated unoccupied density of states (DOS) in pure Ni and TiNi intermetallic compound. Notice the correlation between the peaks of $d$ Ni and $d$ Ti states.

References


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