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## Electronic structure of Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga alloys

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This work investigates the charge transfer and Al (Ga) *p*-Ni *d* hybridization effects in the intermetallic Ni<sub>3</sub>Al (Ni<sub>3</sub>Ga) alloy using the Ni *L*<sub>3,2</sub>- and *K*-edge and Al (Ga) *K* x-ray absorption near edge structure (XANES) measurements. We find that the intensity of white-line features at the Ni *L*<sub>3,2</sub>-edge in the Ni<sub>3</sub>Al (Ni<sub>3</sub>Ga) alloy decreased in comparison with that of pure Ni, which can be attributed to the enhancement of Ni *3d* states filling and the depletion of the density of Ni *3d* unoccupied states in the Ni<sub>3</sub>Al (Ni<sub>3</sub>Ga) alloy. Two clear features are also observed in the Ni<sub>3</sub>Al (Ni<sub>3</sub>Ga) XANES spectrum at the Al (Ga) *K*-edge, which can be assigned to the Al (Ga) unoccupied *3p* (*4p*) states and their hybridized states with the Ni *3d/4sp* states above the Fermi level in Ni<sub>3</sub>Al (Ni<sub>3</sub>Ga). The threshold at Al *K*-edge XANES for Ni<sub>3</sub>Al clearly shifts towards higher photon energies relative to that of pure Al, indicating that Al loses charges upon forming Ni<sub>3</sub>Al. On the other hand, the Ni *K*-edge shifts towards lower photon energies in Ni<sub>3</sub>Al (Ni<sub>3</sub>Ga) relative to that of pure Ni, which is consistent with the results of the Al *K*-edge XANES spectrum and is indicative of a charge transfer from Al to Ni sites. Our data support that no significant *net* charge flow occurs on and off sites in Ni<sub>3</sub>Al (Ni<sub>3</sub>Ga).

**Keywords:** hybridization effect, XANES, charge transfer

### 1. Introduction

The intermetallic Ni<sub>3</sub>Al compound has received extensive attention owing to its potential applications in high-temperature structural materials (Stoloff, 1984). The unique properties of Ni<sub>3</sub>Al compound are principally attributed to the nature of its electronic and atomic structures. Muller *et al.* (1995) performed Ni *L*<sub>3,2</sub>-edge electron energy loss spectroscopy (EELS) to investigate the electronic structure of segregated grain boundaries in Ni<sub>3</sub>Al with boron-doped and undoped conditions. Owing to the absence of a core level shift in the Ni *L*<sub>3</sub>-edge EELS spectra of Ni<sub>3</sub>Al from that of pure Ni, Muller *et al.* concluded that little *net* charge is transferred between Al and Ni sites in Ni<sub>3</sub>Al. On the other hand, Iotova *et al.* (1996) systematically

calculated electronic structures and elastic properties in the series of Ni<sub>3</sub>X (X = Mn, Al, Ga, Ge, and Si) and found an increasing trend of shear module that goes from Ni<sub>3</sub>Mn to Ni<sub>3</sub>Si. This trend could be related to the anisotropic bonding charge density resulting from a combination of the charge transfer from X to Ni and strong X *p*-Ni *d* (Mn *d*-Ni *d* in Ni<sub>3</sub>Mn) hybridization effects in Ni<sub>3</sub>X. Here, we focus on the understanding of how X influences the *p*-*d* hybridization between Al and Ni in Ni<sub>3</sub>Al and between Ga and Ni in Ni<sub>3</sub>Ga and clarification of the controversy over the charge transfer between Al (Ga) and Ni sites in Ni<sub>3</sub>Al (Ni<sub>3</sub>Ga). How charge transfer influences the filling of the Ni *3d* band in Ni<sub>3</sub>Al (Ni<sub>3</sub>Ga) will be addressed.

### 2. Experimental

The XANES measurements were performed using the high-energy spherical grating monochromator (HSGM) with an electron beam energy of 1.5 GeV and a maximum stored current of 200 mA at the Synchrotron Radiation Research Center (SRRC), Hsinchu, Taiwan. The spectra of the Ni *L*<sub>3,2</sub>-edge and Al *K*-edge XANES were measured using the sample drain current mode at the room temperature. The Ni and Ga *K*-edge XANES measurements were also performed in a total electron mode at the wiggler beamline of SRRC. A Si(111) double crystal monochromator was used to record the spectra. The samples were prepared by arc melting after argon backfill, as described elsewhere (Hsu *et al.*, 1996).

### 3. Results and discussion

Figures 1 and 2 display the Ni *L*<sub>3,2</sub>-edge and Al *K*-edge XANES spectra of the Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga alloys, respectively, in which pure Ni and Al metals are given as references. All the spectra shown in these figures were divided by the incident intensity *I*<sub>0</sub> and, then, normalized to an edge jump of unity. By using the dipole-selection transition rule, we can assign the white-line features at the Ni *L*<sub>3,2</sub>-edge (labeled *L*<sub>3</sub> and *L*<sub>2</sub>) XANES to photoelectron transitions from the Ni *2p*<sub>3/2</sub> and *2p*<sub>1/2</sub> ground states to the final unoccupied Ni *3d* electron states. The general spectral lineshapes in the Ni *L*<sub>3,2</sub>-edge XANES spectra of Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga display similar white-line features (labeled A<sub>1</sub>) above the Ni *L*<sub>3</sub>-edge. However, their intensities are reduced in comparison with that of pure Ni. The dependence of the general behavior of the spectra's lineshape and intensity on the photon energy for Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga are similar except that the intensity of the white-line features A<sub>1</sub> (the higher energy satellite structure, B<sub>1</sub>) at Ni *L*<sub>3</sub>-edge is slightly lower (larger) in the Ni<sub>3</sub>Al spectrum than in the Ni<sub>3</sub>Ga spectrum. The difference curves (hereinafter referred to as ΔA<sub>1</sub> and ΔB<sub>1</sub>) of Ni *L*<sub>3</sub>-edge XANES in Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga with respect to pure Ni are shown in the inset of Fig. 1. No significant energy shifts of the highest peak in Ni *L*<sub>3,2</sub>-edge XANES spectra for both alloys from that of pure Ni are observed. Our data are in agreement with earlier Ni *L*<sub>3,2</sub>-edge EELS measurements made on Ni<sub>1-x</sub>Al<sub>x</sub> alloys (Muller *et al.*, 1995). In addition, the satellite structures B<sub>1</sub>, occurring at ~6 eV above the Ni *L*<sub>3</sub>-edge in the XANES spectra of both Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga are enhanced and broadened relative to that of pure Ni. This satellite structure can be assigned to the excitation of Ni *2p*<sub>3/2</sub>

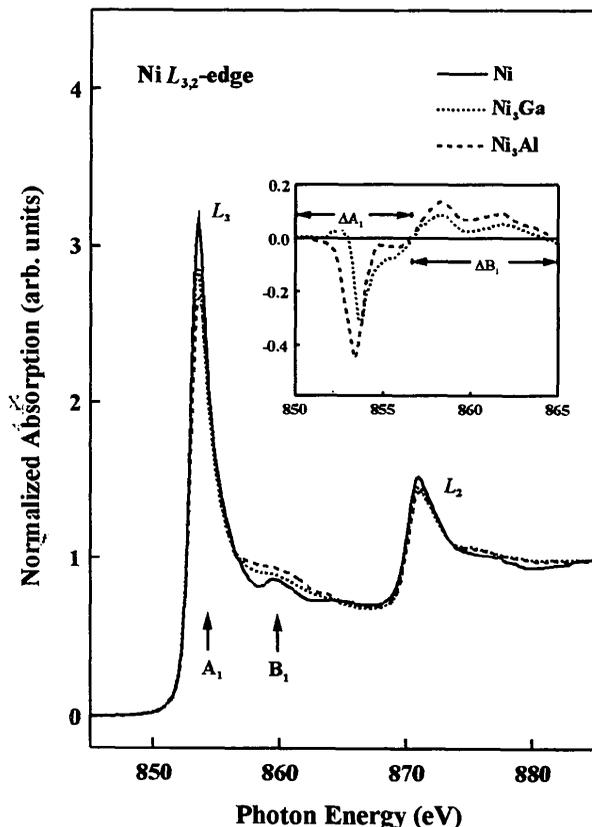


Fig. 1

Normalized Ni  $L_{3,2}$ -edge x-ray absorption spectra of  $\text{Ni}_3\text{Al}$  and  $\text{Ni}_3\text{Ga}$  alloys and pure Ni metal at room temperature. The inset shows the Ni  $L_3$ -edge difference curve for  $\text{Ni}_3\text{Al}$  and  $\text{Ni}_3\text{Ga}$  with respect to pure Ni.

$2p_{3/2}$  photoelectrons to  $4s$  states in the conduction band of Ni (van der Laan *et al.*, 1986 & Chen *et al.*, 1991). Our results obviously indicate a decrease in the intensity of white-line features  $A_1$  at the Ni  $L_3$ -edge for both  $\text{Ni}_3\text{Al}$  and  $\text{Ni}_3\text{Ga}$  alloys relative to that of pure Ni, which can be attributed to the enhancement of Ni  $3d$  states filling that decreases the density of Ni  $3d$  unoccupied states in the alloys.

Fig. 2 displays the Al  $K$ -edge XANES spectra for  $\text{Ni}_3\text{Al}$  and pure Al. In the  $\text{Ni}_3\text{Al}$  spectrum, the intensity of feature  $A_2$ , which is located between  $\sim 1573$  and  $1577$  eV, is reduced. In addition, a prominent feature  $B_2$  (located between  $\sim 1577$  and  $1590$  eV) is significantly enhanced in the  $\text{Ni}_3\text{Al}$  spectrum. The lower inset of this same figure reveals a similar behavior of features  $A_2^*$  and  $B_2^*$  at the Ga  $K$ -edge XANES in the  $\text{Ni}_3\text{Ga}$  spectrum. Furthermore, based on results of the spin-polarized first-principles calculations using the pseudofunction method (Chang *et al.*, 1998), the features  $A_2$  ( $A_2^*$ ) and  $B_2$  ( $B_2^*$ ) in the Al (Ga)  $K$ -edge XANES spectra as shown in the (inset) of Fig. 2 can be assigned to the transitions to Al (Ga) unoccupied  $3p$  ( $4p$ ) states, which have hybridized with the Ni  $3d$ /non- $d$  bands of  $\text{Ni}_3\text{Al}$  ( $\text{Ni}_3\text{Ga}$ ) above the Fermi level. The inflection point in the  $\text{Ni}_3\text{Al}$  XANES spectrum at the Al  $K$ -edge apparently shifts towards higher photon energies than those of pure Al. This

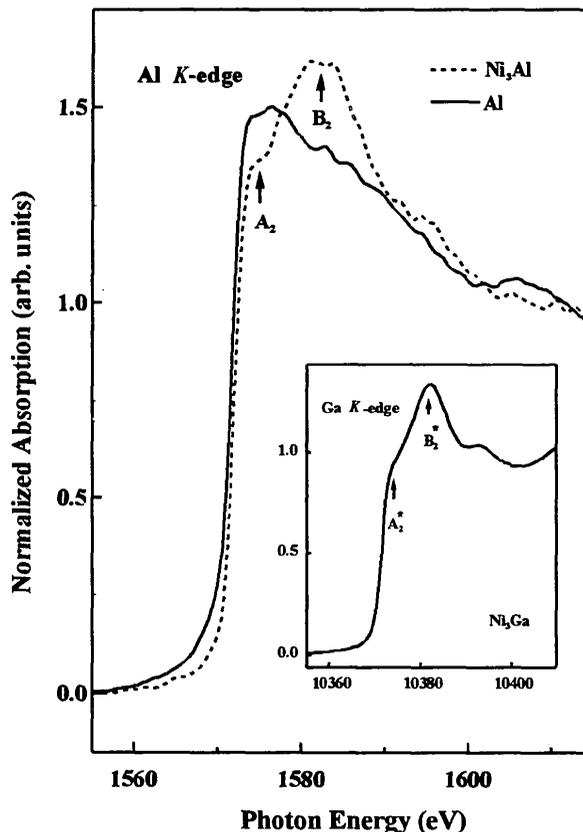
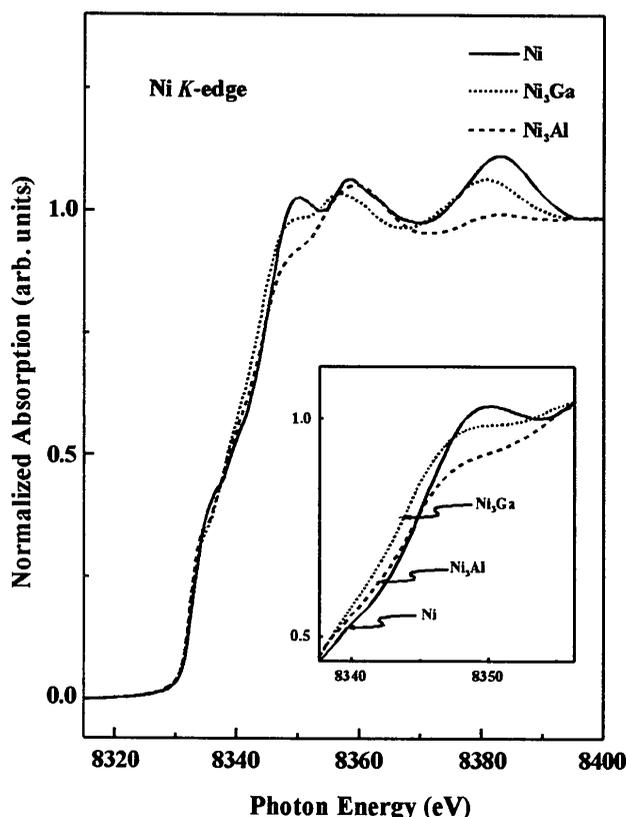


Fig. 2

Normalized Al  $K$ -edge x-ray absorption spectra of  $\text{Ni}_3\text{Al}$  (dot line) and pure Al (solid line) at room temperature. The lower inset shows the normalized Ga  $K$ -edge x-ray absorption spectra of the  $\text{Ni}_3\text{Ga}$  alloy, in which the zero energy was selected at the inflection point of the edge.

suggests that Al loses charge upon forming  $\text{Ni}_3\text{Al}$ . In metals, the charge count at the atomic site (Wigner Seitz volume) tends to remain neutral, *i. e.* only a small amount of *net* charge transfer possibly occurs upon alloying. Although electroneutrality is the general rule, charge redistribution of localized  $d$  electron and itinerant  $sp$  type conduction electrons according to relative electronegativity of the constituent metals in the alloy can still occur without any significant *net* charge flow on and off a site in alloys (Kuhn & Sham, 1994; Sham *et al.*, 1997; Hsieh *et al.*, 1998). The threshold of the  $\text{Ni}_3\text{Al}$  XANES spectrum at the Al  $K$ -edge shifts to higher photon energies in comparison with that of pure Al, which implies that electron transfer occurs from Al to Ni sites because the loss of local  $3p$  electrons reduces the screening of the Al nuclear charge and consequently lowers the  $1s$  core level energy of Al. This finding is consistent with that of the Ni  $L_{3,2}$ -edge XANES spectrum, which is also indicative of the charge transfer from Al to Ni sites in  $\text{Ni}_3\text{Al}$ . Based on the electroneutrality argument (Kuhn & Sham, 1994; Sham *et al.*, 1997; Hsieh *et al.*, 1998), one would intuitively expect that the Ni levels should shift to lower photon energies in  $\text{Ni}_3\text{Al}$  since the positive shift in photon



**Fig. 3**  
Normalized Ni *K*-edge x-ray absorption spectra of the Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga alloys and pure Ni at room temperature. The region of threshold edge in the inset is on a magnified scale.

energy of the Al *p* states in Ni<sub>3</sub>Al tends to be accompanied by the shift of the Ni levels in an opposite direction. However, the Ni *3d* states in Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga did not shift noticeably towards lower photon energies at Ni *L*<sub>3,2</sub>-edge, as shown in Fig. 1. Thus, we argue that the charge transfer or charge flow occurs not only through the Al *3p* (Ga *4p*)-Ni *3d* hybridized states, but also through the rehybridized *s-p-d* states involving one or two sites in Ni<sub>3</sub>Al (Ni<sub>3</sub>Ga). The involvement of conduction electrons of Ni *p* character in rehybridization can be revealed from the Ni *K*-edge XANES, which probes the unoccupied Ni *4p* states above the Fermi level.

Fig. 3 displays the Ni *K*-edge XANES of Ni<sub>3</sub>Al, Ni<sub>3</sub>Ga, and pure Ni. The absorption intensity above the main edge decreases noticeably and the shift of the main edge towards the lower photon energies for both Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga is comparable with that of pure Ni (refer to the inset of Fig. 3). The pre-edge shoulder in the Ni *K*-edge XANES can be attributed to the Ni *1s* → *3d* transition facilitated by band formation and Ni *p-d* rehybridization (Kuhn & Sham, 1994; Sham *et al.*, 1997; Hsieh *et al.*, 1998). A reduction of the Ni *K* near edge intensity suggests that Ni *4p* orbitals gain electron charges upon alloying in Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga. Correspondingly, Ni must loss *s* electron charges in both Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga for metallic systems tend to maintain charge neutrality locally.

Thus, the density of unoccupied Ni *s* states in the vicinity of the Fermi level will increase in both Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga relative to that of pure Ni. This indeed can be observed in the satellite structure B<sub>1</sub> at the Ni *L*<sub>3</sub>-edge of the XANES spectra for Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga as shown in Fig. 1, which can be seen to be relatively dispersive and stronger. This observation is consistently supported by the observed difference curves of the Ni *L*<sub>3</sub>-edge spectra between alloys and Ni as shown in the inset of Fig. 1. Under the framework of local electron conservation or compensation argument, our results indicate that the larger negative integrated intensity of ΔA<sub>1</sub> (indicating that Ni *3d* orbitals gain more electron charges) implies a larger positive integrated intensity of ΔB<sub>1</sub> (indicating that Ni *4s* orbital loses more electron charges) in Ni<sub>3</sub>Al and Ni<sub>3</sub>Ga. We did not discuss Ni *p* orbital charges because *s* electrons are more important than *p* electrons in these metallic systems and its effect can be implicitly included in the *d* orbitals. Our data support that no significant *net* charge flow occurs on and off sites in Ni<sub>3</sub>Al (Ni<sub>3</sub>Ga).

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