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Electronic structure of Ni₃Al and Ni₃Ga alloys

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This work investigates the charge transfer and Al (Ga) *p*-Ni *d* hybridization effects in the intermetallic Ni₃Al (Ni₃Ga) alloy using the Ni *L*_{3,2}- 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*_{3,2}-edge in the Ni₃Al (Ni₃Ga) 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 Ni₃Al (Ni₃Ga) alloy. Two clear features are also observed in the Ni₃Al (Ni₃Ga) 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 Ni₃Al (Ni₃Ga). The threshold at Al *K*-edge XANES for Ni₃Al clearly shifts towards higher photon energies relative to that of pure Al, indicating that Al loses charges upon forming Ni₃Al. On the other hand, the Ni *K*-edge shifts towards lower photon energies in Ni₃Al (Ni₃Ga) 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 Ni₃Al (Ni₃Ga).

Keywords: hybridization effect, XANES, charge transfer

1. Introduction

The intermetallic Ni₃Al compound has received extensive attention owing to its potential applications in high-temperature structural materials (Stoloff, 1984). The unique properties of Ni₃Al compound are principally attributed to the nature of its electronic and atomic structures. Muller *et al.* (1995) performed Ni *L*_{3,2}-edge electron energy loss spectroscopy (EELS) to investigate the electronic structure of segregated grain boundaries in Ni₃Al with boron-doped and undoped conditions. Owing to the absence of a core level shift in the Ni *L*₃-edge EELS spectra of Ni₃Al from that of pure Ni, Muller *et al.* concluded that little *net* charge is transferred between Al and Ni sites in Ni₃Al. On the other hand, Iotova *et al.* (1996) systematically

calculated electronic structures and elastic properties in the series of Ni₃X (X = Mn, Al, Ga, Ge, and Si) and found an increasing trend of shear module that goes from Ni₃Mn to Ni₃Si. 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 Ni₃Mn) hybridization effects in Ni₃X. Here, we focus on the understanding of how X influences the *p*-*d* hybridization between Al and Ni in Ni₃Al and between Ga and Ni in Ni₃Ga and clarification of the controversy over the charge transfer between Al (Ga) and Ni sites in Ni₃Al (Ni₃Ga). How charge transfer influences the filling of the Ni *3d* band in Ni₃Al (Ni₃Ga) 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*_{3,2}-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*_{3,2}-edge and Al *K*-edge XANES spectra of the Ni₃Al and Ni₃Ga 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*₀ 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*_{3,2}-edge (labeled *L*₃ and *L*₂) XANES to photoelectron transitions from the Ni *2p*_{3/2} and *2p*_{1/2} ground states to the final unoccupied Ni *3d* electron states. The general spectral line shapes in the Ni *L*_{3,2}-edge XANES spectra of Ni₃Al and Ni₃Ga display similar white-line features (labeled A₁) above the Ni *L*₃-edge. However, their intensities are reduced in comparison with that of pure Ni. The dependence of the general behavior of the spectra's line shape and intensity on the photon energy for Ni₃Al and Ni₃Ga are similar except that the intensity of the white-line features A₁ (the higher energy satellite structure, B₁) at Ni *L*₃-edge is slightly lower (larger) in the Ni₃Al spectrum than in the Ni₃Ga spectrum. The difference curves (hereinafter referred to as ΔA₁ and ΔB₁) of Ni *L*₃-edge XANES in Ni₃Al and Ni₃Ga with respect to pure Ni are shown in the inset of Fig. 1. No significant energy shifts of the highest peak in Ni *L*_{3,2}-edge XANES spectra for both alloys from that of pure Ni are observed. Our data are in agreement with earlier Ni *L*_{3,2}-edge EELS measurements made on Ni_{1-x}Al_x alloys (Muller *et al.*, 1995). In addition, the satellite structures B₁, occurring at ~6 eV above the Ni *L*₃-edge in the XANES spectra of both Ni₃Al and Ni₃Ga are enhanced and broadened relative to that of pure Ni. This satellite structure can be assigned to the excitation of Ni *2p*_{3/2}

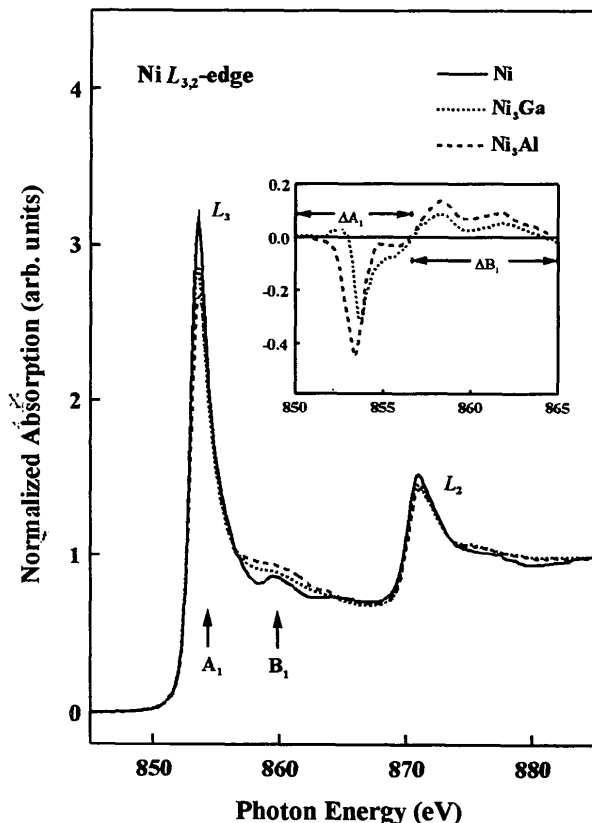


Fig. 1

Normalized Ni $L_{3,2}$ -edge x-ray absorption spectra of Ni_3Al and Ni_3Ga alloys and pure Ni metal at room temperature. The inset shows the Ni L_3 -edge difference curve for Ni_3Al and Ni_3Ga 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 Ni_3Al and Ni_3Ga 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 Ni_3Al and pure Al. In the Ni_3Al spectrum, the intensity of feature A_2 , which is located between ~ 1573 and 1577 eV, is reduced. In addition, a prominent feature B_2 (located between ~ 1577 and 1590 eV) is significantly enhanced in the Ni_3Al 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 Ni_3Ga 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 Ni_3Al (Ni_3Ga) above the Fermi level. The inflection point in the Ni_3Al XANES spectrum at the Al K -edge apparently shifts towards higher photon energies than those of pure Al. This

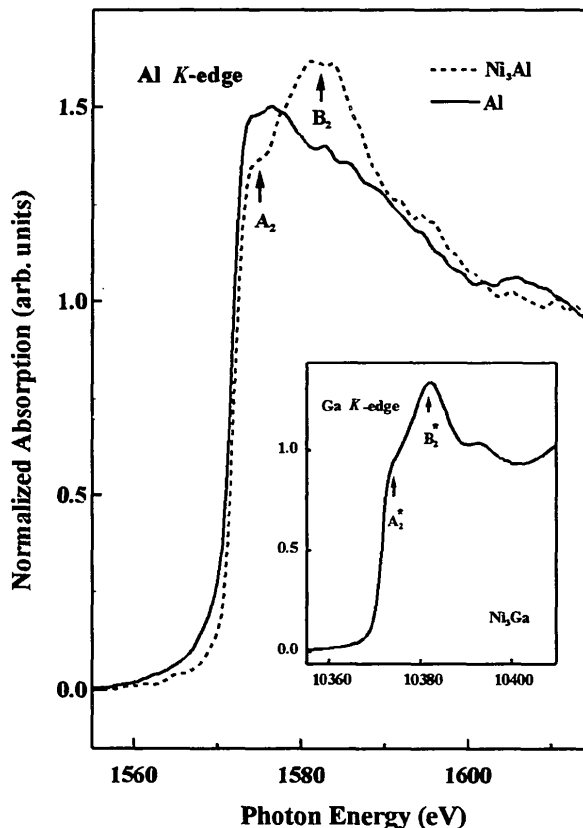


Fig. 2

Normalized Al K -edge x-ray absorption spectra of Ni_3Al (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 Ni_3Ga alloy, in which the zero energy was selected at the inflection point of the edge.

suggests that Al loses charge upon forming Ni_3Al . 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 Ni_3Al 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 Ni_3Al . 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 Ni_3Al since the positive shift in photon

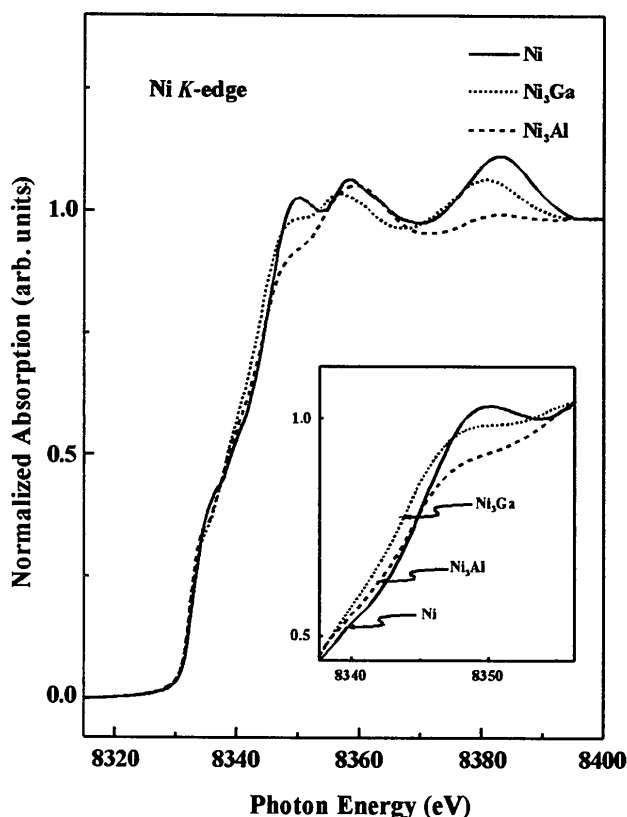


Fig. 3
Normalized Ni *K*-edge x-ray absorption spectra of the Ni_3Al and Ni_3Ga alloys and pure Ni at room temperature. The region of threshold edge in the inset is on a magnified scale.

energy of the Al *p* states in Ni_3Al tends to be accompanied by the shift of the Ni levels in an opposite direction. However, the Ni *3d* states in Ni_3Al and Ni_3Ga did not shift noticeably towards lower photon energies at Ni $L_{3,2}$ -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_3Al (Ni_3Ga). 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_3Al , Ni_3Ga , 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_3Al and Ni_3Ga 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 $1s \rightarrow 3d$ 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_3Al and Ni_3Ga . Correspondingly, Ni must loss *s* electron charges in both Ni_3Al and Ni_3Ga 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_3Al and Ni_3Ga relative to that of pure Ni. This indeed can be observed in the satellite structure B_1 at the Ni L_3 -edge of the XANES spectra for Ni_3Al and Ni_3Ga 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_3 -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_1 (indicating that Ni *3d* orbitals gain more electron charges) implies a larger positive integrated intensity of ΔB_1 (indicating that Ni *4s* orbital loses more electron charges) in Ni_3Al and Ni_3Ga . 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_3Al (Ni_3Ga).

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