Experimental and theoretical study of the electronic structures of intermetallic compounds and alloys containing Fe or Ni

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Abstract

The electronic structures of two groups of intermetallic compounds and alloys containing Fe, V, or Ni are studied by X-ray absorption near-edge spectra (XANES) at the Fe, V, and Ni $L_{2,3}$ edges and the Fe K edge. The XANES spectra are compared with those calculated with two theoretical methods. The differences in the XANES spectra of compounds containing Ni calculated by these two methods are discussed. Except for NiGa, a reasonable good agreement between theory and experiment was found for all materials. The density of states at the Fermi energy at different atomic sites are also calculated for the compounds and alloys containing Fe.

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1. Introduction

Intermetallic compounds and alloys that contain transition metals and a group-III metal display interesting mechanical, electronic, magnetic, transport, and optical properties. In this paper, X-ray absorption near-edge spectra (XANES) at the Fe, V, and Ni $L_{2,3}$ edges of two groups of intermetallic compounds and alloys were measured and compared with theoretical XANES spectra. These two groups of samples are: (1) Fe_3Al , Fe_2VAl , and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0, 0.02, 0.05$, and 0.11), and (2) Ni_3Al , Ni_3Ga , Ni_3In , and NiGa . The Fe K-edge XANES spectra of $\text{Fe}_{1.98}\text{V}_{1.02}\text{Al}$ and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0.02, 0.05$, and 0.11) are also reported and compared with theoretical spectra in this paper. The crystal structures and Curie temperatures of the seven stoichiometric compounds are listed in Table 1. While Fe_3Al is classified as a ferromagnetic metal, the Heusler-type compounds Fe_2VAl and Fe_2VGa are characterized as semimetals due to a deep pseudogap formation right at the Fermi energy (E_F). The presence of this sharp pseudogap of the size of several tenth

of an eV was predicted by several theoretical band-structure calculations and further confirmed by various experimental measurements [1]. When one replaces Fe(I) atoms by V atoms in Fe_2VAl and Fe_2VGa , the low-temperature electrical resistivity and thermoelectric power increase drastically [1]. This thermopower enhancement for Fe_2VAl is caused by a sharp rise of the density of state (DOS) in both sides of the pseudogap [2]. This observation suggests that both systems contain fewer charge carriers and behave semimetallically. Tunability of the physical characteristic of Fe_2VAl by doping V at the specific Fe site is also found in its magnetic and transport properties [3]. Moreover, Fe_2VAl and Fe_2VGa have been reported to be possible 3d heavy-fermion materials [3,4]. The ordered compounds Fe_3Al , Ni_3Al , and Ni_3Ga have many unique properties that make them attractive for high-temperature, corrosion-resistant, and super-hard applications, while NiGa possesses complicated defect structure and has been suggested as a potential conducting contact to III–V semiconductors [5].

Experimental and theoretical Fe and V K-edge XANES spectra of Fe_3Al , Fe_2VAl , and Fe_2VGa were published recently [6,7]. To our knowledge, no Fe and V $L_{2,3}$ -edge XANES spectra can be found in the literature for these three compounds and the disordered alloys $\text{Fe}_{2-x}\text{V}_{1+x}\text{X}$ (X: Al,

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Table 1

Crystal structures and Curie temperatures (T_C) for Ni_3Al , Ni_3Ga , Ni_3In , NiGa , Fe_3Al , Fe_2VAl , and Fe_2VGa

Material	Crystal structure	T_C (K)
Ni_3Al	L1_2	41.5
Ni_3Ga	L1_2	
Ni_3In	L1_2	
NiGa	B2	
Fe_3Al	D0_3	713
Fe_2VAl	L2_1	
Fe_2VGa	L2_1	

Ga). Experimental Ni $\text{L}_{2,3}$ -edge and Al and Ni K-edge XANES spectra of Ni_3Al , [8–14] Ni_3Ga , [9–11,13–15] Ni_3In , [11,13,14,16] and NiGa [11,13,15] have been reported previously. The Ni $\text{L}_{2,3}$ near-edge structures of Ni_3Al were also measured by electron-energy-loss spectroscopy [17,18]. Theoretical analyses of the Ni $\text{L}_{2,3}$ -edge and Al and Ni K-edge XANES spectra have been performed on Ni_3Al , [10–14] Ni_3Ga , [10,11,13,14] Ni_3In , [11,13,14,16] and NiGa [11,13] using several methods. The purpose of this paper is to systematically study the electronic structures of a series of technologically interesting intermetallic compounds and alloys, and to compare with available experimental and theoretical results. The total and site-decomposed DOSs at E_F ($n(E_F)$) of the Heusler-type compounds and alloys are also calculated. We note that very few studies were performed on the doped alloys $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$. Not many reports are found for Ni_3In and NiGa , either.

This paper is organized as follows. In Section 2 the experimental and the theoretical methods are described. In Section 3 the results and discussion are presented. The conclusions of this work are contained in Section 4.

2. Methods

2.1. Experimental methods

Preparation and characterization of polycrystalline samples of the Fe or Ni intermetallic compounds and alloys were reported previously [1,7,8,19]. The XANES experiments on Ni $\text{L}_{2,3}$, Fe and V $\text{L}_{2,3}$, and Fe K edges were carried out on beam lines 12A, 15A, and 15B, respectively, at the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The XANES spectra were collected at room temperature by recording the total yield of secondary electrons at beam lines 12A and 15A and the fluorescence yield at beam line 15B. We note that the XANES spectra taken by using the fluorescence-yield mode is more bulk sensitive than those taken by the using the total-electron-yield mode. Standard 5 μm thick Fe, V, and Ni foils were used as a reference for energy calibration and their XANES data were also used as reference spectra. The photon flux was obtained simultaneously by measuring the current of a Au

mesh located near the exit slit of the monochromator and used for normalization of the XANES spectra. For the Fe and V $\text{L}_{2,3}$ -edge XANES measurements, the samples were scraped with a diamond file and annealed to 500 °C until photoemission spectra showed no O and C contamination on the sample surfaces. Since Al_2O_3 cannot be completely removed from the surfaces of the alloys $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ ($x = 0.02, 0.05$, and 0.11), we thus only report here the XANES spectra of the $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0, 0.02, 0.05$, and 0.11) compound and alloys. On the other hand, clean surfaces can be obtained by ion-bombardment and subsequent annealing to 500 °C for Ni_3Al , Ni_3Ga , Ni_3In , and NiGa . The metalloid deficiency after cyclic Ar-ion sputtering and annealing ranges from 5 to 25% for these four intermetallic compounds [11].

2.2. Theoretical methods

The theoretical XANES spectra of these intermetallic compounds and alloys are calculated using two methods. The first is the all-electron full-potential linear augmented-plane-wave (FLAPW) method, [20] and the second is the multiple scattering (MS) method [21]. Details of these two calculations were published previously [6,11,13,16]. The FLAPW calculation is based on first-principles density functional theory with the generalized gradient approximation (GGA) to the exchange-correlation potential. We find that using the GGA is essential to bring the calculated lattice constants and bulk moduli of these compounds into good agreement with the experimental values. We note that GGA is more accurate than local spin-density approximation in calculating the electronic structures of Fe_2VAl and Fe_2VGa [4,6]. The FLAPW calculations are done for the paramagnetic or ferromagnetic state for the Fe, V, or Ni $\text{L}_{2,3}$ -edge and Fe K-edge XANES spectra of these materials. The effect of V substitution of the Fe(I) atoms was taken into account by the virtual-crystal approximation (VCA) in which the V–Fe(I) sites were occupied by virtual atoms whose atomic number (Z) is $Z = (1 - x/2)Z(\text{Fe}) + (x/2)Z(\text{V})$. The VCA has been found to be applicable for many metallic alloys with similar atomic numbers [22,23]. The MS method is based on a self-consistent-field, single-electron, ab-initio real space Green's function code FEFF8. The MS calculations are performed in the absence of a core hole for the Ni $\text{L}_{2,3}$ -edge XANES spectra of Ni_3Al , Ni_3Ga , Ni_3In , and NiGa . These spectra are compared with those calculated by the FLAPW method.

3. Results and discussions

3.1. Fe and V $\text{L}_{2,3}$ -edge XANES spectra of Fe_3Al , Fe_2VAl , and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0, 0.02, 0.05$, and 0.11)

The experimental (open circles) and theoretical (solid line) XANES spectra of Fe $\text{L}_{2,3}$ edges for Fe_3Al , Fe_2VAl ,

Fig. 1. The experimental (○) and theoretical (—) Fe $L_{2,3}$ -edge XANES spectra for (a) Fe_3Al , (b) Fe_2VAl , (c) Fe_2VGa , (d) $\text{Fe}_{1.98}\text{V}_{1.02}\text{Ga}$, (e) $\text{Fe}_{1.95}\text{V}_{1.05}\text{Ga}$, and (f) $\text{Fe}_{1.89}\text{V}_{1.11}\text{Ga}$.

Fig. 2. Same as in Fig. 1, except for V $L_{2,3}$ -edge for (a) Fe_2VAl , (b) $\text{Fe}_{1.98}\text{V}_{1.02}\text{Ga}$, (c) $\text{Fe}_{1.95}\text{V}_{1.05}\text{Ga}$, and (d) $\text{Fe}_{1.89}\text{V}_{1.11}\text{Ga}$.

and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0, 0.02, 0.05$, and 0.11) are shown in Fig. 1a–f, respectively. The XANES spectrum for Fe_3Al is obtained from the spin-polarized calculation, while those for other materials are obtained from paramagnetic calculations. Those of V $L_{2,3}$ edges for Fe_2VAl and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0.02, 0.05$, and 0.11) are shown in Fig. 2a–d, respectively. The theoretical spectra were calculated using the FLAPW method. The zero energy corresponds to the inflection point of the respective Fe or V L_3 absorption edge (706.8 and 512.1 eV, respectively). The experimental data were normalized to the theoretical spectra at the peak of the Fe or V L_3 edge. The agreement between theory and experiment for the Fe $L_{2,3}$ -edge XANES spectra is best for Fe_3Al and Fe_2VAl , good for Fe_2VGa and $\text{Fe}_{1.95}\text{V}_{1.05}\text{Ga}$, and worse for $\text{Fe}_{1.98}\text{V}_{1.02}\text{Ga}$ and $\text{Fe}_{1.89}\text{V}_{1.11}\text{Ga}$; while it is worse for the V $L_{2,3}$ -edge spectra for Fe_2VAl and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0.02, 0.05$, and 0.11). The decrease in intensity above the Fe or V L_2 -edge peak is due to the finite-sized, linearized energy-dependent basis sets in the muffin-tin spheres used in the FLAPW calculation. This effect may also cause the decrease of the theoretical Fe and V L_2 -edge peak height

for $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0.02$ and 0.11) and the four materials shown in Fig. 2, respectively. Another source of error is that the GGA eigenvalues are not the true excitations of the XANES spectra, and the error in peak position is comparable to the self-energy correction between GGA and more sophisticated methods such as GW [24]. The third source of error may come from the use of VCA approximation for the $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ alloys.

3.2. Fe and V K-edge XANES spectra of $\text{Fe}_{1.98}\text{V}_{1.02}\text{Al}$ and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0.02, 0.05$, and 0.11)

We performed both the spin-polarized and the non-spin-polarized calculations for these alloys, no difference in total energy was found between these two calculations. Thus, these four materials are nonmagnetic and the theoretical XANES spectra calculated by the FLAPW method of the paramagnetic state are used for comparing with the experimental ones. The theoretical and experimental lattice constants of these alloys are shown in the third column in Table 2. Slight increase in the lattice constants is found

Table 2

Lattice constant a , total density of states at the Fermi energy $n(E_F)$, and bulk modulus B for Fe_2VAl , Fe_2VGa , $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$, and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0.02, 0.05$, and 0.11)

Material		a (Å)	$n(E_F)$ (states/eV cell)	B (Mbar)
Fe_2VAl	Para	5.712	0.18	2.12
	Exp.	5.76		
$\text{Fe}_{1.98}\text{V}_{1.02}\text{Al}$	Para.	5.713	0.629	2.121
	Exp.	5.763		
$\text{Fe}_{1.95}\text{V}_{1.05}\text{Al}$	Para.	5.715	1.776	2.117
	Exp.	5.763		
$\text{Fe}_{1.89}\text{V}_{1.11}\text{Al}$	Para.	5.720	3.287	2.114
	Exp.	5.763		
Fe_2VGa	Para.	5.726	0.28	2.14
	Exp.	5.77		
$\text{Fe}_{1.98}\text{V}_{1.02}\text{Ga}$	Para.	5.726	0.436	2.141
	Exp.	5.776		
$\text{Fe}_{1.95}\text{V}_{1.05}\text{Ga}$	Para.	5.727	0.894	2.141
	Exp.	5.777		
$\text{Fe}_{1.89}\text{V}_{1.11}\text{Ga}$	Para.	5.731	3.431	2.140
	Exp.	5.786		

Para. and Exp. represent theoretical paramagnetic and experimental values, respectively.

as V atoms substitute into the Fe(I) sites. For Fe_2VAl and Fe_2VGa , doping V atoms at the Fe(I) positions results in lower total energy than doping V atoms at both the Fe(I) and Fe(II) positions. This is consistent with the well-known site-selectivity property of the Heusler-type compounds, and was confirmed theoretically for Fe_2VSi [3]. Since Fe(I) is less electronegative than Fe(II), the Coulomb energy of the crystal lattice will be reduced if Fe(I) is replaced by a less electronegative element V. This explains the observed site selectivity of the Heusler-type compounds.

The experimental (open circles) and theoretical (solid lines) XANES spectra of Fe K edge for $\text{Fe}_{1.98}\text{V}_{1.02}\text{Al}$, $\text{Fe}_{1.98}\text{V}_{1.02}\text{Ga}$, $\text{Fe}_{1.95}\text{V}_{1.05}\text{Ga}$, and $\text{Fe}_{1.89}\text{V}_{1.11}\text{Ga}$ are depicted in Fig. 3a–d, respectively. Also shown in Fig. 3 are the Fe p partial DOS (dots) convoluted by the experimental resolution of 1 eV for these alloys. The corresponding XANES spectra of V K edge and V p partial DOS for these four alloys are depicted in Fig. 4a–d, respectively. The maxima of the experimental XANES spectra in Figs. 3 and 4, which correspond to Fe or V 1s to ϵp transitions, coincide with the peaks in the Fe and V p partial DOS curves, respectively. The zero energies in Figs. 3 and 4

Fig. 3. The experimental (○) and theoretical (—) Fe K-edge XANES spectra for (a) $\text{Fe}_{1.98}\text{V}_{1.02}\text{Al}$, (b) $\text{Fe}_{1.98}\text{V}_{1.02}\text{Ga}$, (c) $\text{Fe}_{1.95}\text{V}_{1.05}\text{Ga}$, and (d) $\text{Fe}_{1.89}\text{V}_{1.11}\text{Ga}$. Also shown is the Fe p partial DOS (···) for these alloys.

Fig. 4. Same as in Fig. 3, except for V K-edge for (a) $\text{Fe}_{1.98}\text{V}_{1.02}\text{Al}$, (b) $\text{Fe}_{1.98}\text{V}_{1.02}\text{Ga}$, (c) $\text{Fe}_{1.95}\text{V}_{1.05}\text{Ga}$, and (d) $\text{Fe}_{1.89}\text{V}_{1.11}\text{Ga}$. Also shown is the V p partial DOS (····) for these alloys.

correspond to the inflection points of the Fe and V K-edge absorption thresholds (7112.1 and 5465 eV, respectively). The experimental data were normalized to the theoretical spectra at the Fe or V K-edge peak. The white-line positions and intensities and the absorption peaks above the white-line energies are well reproduced in the theoretical spectra. Discrepancies in peak positions and peak intensities between theoretical and experimental spectra might be due to the use of the GGA approximation in density functional theory and to the neglect of the core-hole effects. Another source of error in peak positions is the self-energy correction between GGA and more sophisticated methods, such as GW [24]. The decrease in peak height after the maxima in the theoretical XANES spectra is due to the finite-sized, linearized energy-dependent basis sets in the muffin-tin spheres used in the present calculation. As for the source of the discrepancy in peak width, the hot-electron lifetime is strongly energy dependent so that it mostly damps peaks about 20 eV above the absorption edge.

The calculated total $n(E_F)$ values for Fe_2VAl , Fe_2VGa , $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$, and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0.02, 0.05$, and 0.11) are listed in the fourth column in Table 2, and the site-decomposed $n(E_F)$ values are listed in Table 3. The cal-

culated $n(E_F)$ values for Fe_2VAl and Fe_2VGa are 0.18 and 0.28 states/eV cell, respectively, and the major contribution to the higher $n(E_F)$ value for Fe_2VGa comes from that of the V sites in this compound, as can be seen in Table 3. Our calculated total and partial $n(E_F)$ values for Fe_2VAl and Fe_2VGa were published previously and compared with those obtained from other theoretical calculations and nuclear magnetic resonance or specific-heat measurements [6]. The calculated total $n(E_F)$ values increase sharply as V

Table 3

Density of states at the Fermi energy $n(E_F)$ (states/eV cell) at different atomic sites for Fe_2VAl , Fe_2VGa , $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$, and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Ga}$ ($x = 0.02, 0.05$, and 0.11)

Material	Fe(I)	Fe(II)	V	Al (Ga)	Interstitial	Total
Fe_2VAl	0.096		0.062	0.007	0.017	0.18
$\text{Fe}_{1.98}\text{V}_{1.02}\text{Al}$	0.270	0.272	0.028	0.020	0.039	0.629
$\text{Fe}_{1.95}\text{V}_{1.05}\text{Al}$	0.793	0.804	0.054	0.039	0.086	1.776
$\text{Fe}_{1.89}\text{V}_{1.11}\text{Al}$	1.448	1.514	0.103	0.065	0.157	3.287
Fe_2VGa	0.119		0.128	0.008	0.024	0.28
$\text{Fe}_{1.98}\text{V}_{1.02}\text{Ga}$	0.182	0.183	0.030	0.013	0.028	0.436
$\text{Fe}_{1.95}\text{V}_{1.05}\text{Ga}$	0.388	0.394	0.038	0.024	0.05	0.894
$\text{Fe}_{1.89}\text{V}_{1.11}\text{Ga}$	1.528	1.596	0.102	0.057	0.148	3.431

doping increase from 0.02 to 0.11 for Fe_2VAl and Fe_2VGa . This is because about 34 and 46% of the total $n(E_F)$ for Fe_2VAl and Fe_2VGa , respectively, comes from the V contribution. The former is close to that (42%) calculated for Fe_2VAl previously [25]. However, for the nonstoichiometric compounds, only a few percent and close to 90% of the total electronic states at E_F arises from V and $\text{Fe(I)} + \text{Fe(II)}$ atoms, respectively (see Table 2). The $n(E_F)$ values at the Fe(I) sites are smaller than those at the Fe(II) sites.

The calculated bulk modulus (B) values for these materials are listed in the last column in Table 2. The B value for the Al compounds decreases slightly as V content increases; while it is essentially a constant for the Ga compounds. To our knowledge, there are no experimental B values reported for these materials.

3.3. Ni $L_{2,3}$ -edge XANES spectra of Ni_3Al , Ni_3Ga , Ni_3In , and NiGa

The experimental (open circles) and theoretical (solid or dashed lines) XANES spectra of Ni $L_{2,3}$ edges for paramagnetic Ni_3Al , Ni_3Ga , Ni_3In , and NiGa are displayed in

Fig. 5a–d, respectively. The theoretically-calculated FLAPW and MS spectra are shown in the lower and upper part, respectively, of each figure. The zero energy corresponds to the inflection point of the Ni L_3 absorption edge (852.7 eV). The experimental data were normalized to the theoretical spectra at the Ni L_3 -edge peak except for Fig. 5d curve (I) of NiGa , whose experimental XANES spectrum was normalized to the theoretical one at the Ni L_2 -edge peak. We note that Ni_3Al , Ni_3Ga , and Ni_3In have the cubic $L1_2$ structure, while NiGa has the B2 structure. It was also reported [26] that Ni_3In has the ordered D0_{19} structure isotypic with Ni_3Sn . However, the Ni $L_{2,3}$ XANES spectrum of Ni_3In calculated with the MS theory using this latter structure resulted in a much worse agreement with the experimental spectrum than using the cubic $L1_2$ structure for Ni_3In [11]. Moreover, calculation using FLAPW theory predicted that nonmagnetic Ni_3In favors energetically the D0_{22} structure rather than the $L1_2$ structure, while ferromagnetism would make the $L1_2$ structure slightly lower in energy than the D0_{22} structure [16]. Thus, in Fig. 5c, the three structures $L1_2$, D0_{22} , and D0_{19} for Ni_3In are used in the FLAPW theory, while only the $L1_2$ structure is used for the MS theory.

Fig. 5. The experimental (○) and theoretical paramagnetic (—) Ni $L_{2,3}$ -edge XANES spectra for (a) Ni_3Al , (b) Ni_3Ga , (c) Ni_3In , and (d) NiGa .

For NiGa, the calculated spectrum with and without multiple scattering is shown as solid and dashed line, respectively, in Fig. 5d. For other three compounds, the spectra are calculated with inclusion of multiple scattering, since without it their theoretical spectra possess no small features above the Ni L₃ white line.

Overall, we have a reasonable good agreement between theoretical and experimental XANES spectra for Ni₃Al and Ni₃Ga. The decrease in peak height roughly 10 eV above the Ni L₃ edge for Ni₃Al and Ni₃Ga is due to the finite-sized, linearized energy-dependent basis sets in the muffin-tin spheres used in the FLAPW calculation. Better agreement with experimental XANES spectra, especially for the Ni L₂ edge, is found for the spectra calculated by the MS method. We note that the peak energy of the Ni L₂ edge calculated by the FLAPW method for Ni₃Al and Ni₃Ga is lower by 0.3 eV and higher by 0.7 eV than the respective experimental values. We also note that the present experimental XANES spectra for Ni₃Al and Ni₃Ga are different from those reported previously [9,10]. Considering the agreement between present experimental and theoretical spectra, we suspect that previous XANES spectra for these two materials are not correct because the sample surfaces were not cleaned well. For Ni₃In, the agreement between theoretical FLAPW and experimental XANES spectra is best for the L1₂ structure, good for the D0₁₉ structure, and fair for the D0₂₂ structure. This observation is different from that found for the Ni K-edge XANES spectra for these three structures, where the D0₂₂ structure possesses the best agreement between the theoretical and experimental spectra [16]. We note that the difference in the Ni K-edge XANES spectra for the three structures of Ni₃In is quite small for a clear identification of which structure is the best one. Both the FLAPW- and MS-calculated XANES spectra for the L1₂ structure of Ni₃In agree well with the experimental one. However, the 6.0 eV peak above the Ni L₃ edge of Ni₃In is better reproduced by the FLAPW method than the MS method. This means that although the MS method is better than the FLAPW method in calculating the high-energy L₂ peak for these compounds, the L₃-edge feature is better reproduced by the FLAPW method due to the use of full potential. All major features of the experimental absorption peaks, as well as white-line positions and intensities, are well reproduced in the theoretical XANES spectra for Ni₃Al, Ni₃Ga, and Ni₃In. For example, the theoretical Ni L_{2,3}-edge XANES spectra for Ni₃Al roughly reproduce the three experimental peaks at 4.2, 7.1, and 9.5 eV above the Ni L₃ white line. The same features are present in the calculated Ni L_{2,3}-edge XANES spectra for Ni₃In, though less pronounced and less agreement with the experimental peak positions at 4.5, 6.0, and 10.0 eV above the Ni L₃ white line. Another source of error in peak positions comes from the use of the GGA approximation in the FLAPW method [24]. As for the source of the discrepancy in peak width, the hot-electron lifetime is strongly energy dependent so that it mostly damps peaks about 20 eV above the absorption edge. Small discrepancies in peak positions and intensities

in the MS calculation might be due to the use of muffin-tin approximation for the potentials. As shown in Fig. 5d (curve D), the MS theory underestimates the Ni L₃ peak intensity of NiGa by about 20%, and the XANES spectrum calculated without using multiple scattering is in better agreement with the experimental data than that calculated with the multiple scattering included. However, compared with the XANES spectrum of NiGa calculated by the FLAPW method, the MS calculation seems more suitable in calculating the electronic structures of materials with high structural disorder like NiGa. The disagreement between theoretical and experimental XANES spectra found for NiGa is caused by high concentration of anti-structure defects (0.75 at.%) present in the sample, [27] which was not considered in the FLAPW method and was not treated adequately in the MS method.

4. Conclusions

The electronic structures of Fe₃Al, Fe_{2-x}V_{1+x}Al, Fe_{2-x}V_{1+x}Ga ($x = 0, 0.02, 0.05$, and 0.11), Ni₃Al, Ni₃Ga, Ni₃In, and NiGa were studied jointly by XANES measurements and by theoretical analysis using the FLAPW and MS methods. The experimental XANES spectra were measured at the Fe, V, and Ni L_{2,3} edges and the Fe K edge. The experimental K-edge XANES features for the Fe compounds and alloys reflect the Fe- and V-p unoccupied DOS, and their $n(E_F)$ values at different atomic sites are calculated. Except for NiGa, a reasonable good agreement between theory and experiment was found for these materials. The disagreement between experimental and theoretical XANES spectra found for NiGa is caused by high concentration of anti-structure defects present in the sample.

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References

- [1] C.-S. Lue, Y.-K. Kuo, Phys. Rev. B 66 (2002) 085121, references therein.
- [2] Y. Nishino, H. Kato, M. Kato, U. Mizutani, Phys. Rev. B 63 (2001) 233303, references therein.
- [3] A. Bansil, S. Kaprzyk, P.E. Mijnarends, J. Tobola, Phys. Rev. B 60 (1999) 13396, references therein.
- [4] G.Y. Guo, G.A. Botton, Y. Nishino, J. Phys.: Condens. Matter 10 (1998) L119.
- [5] T. Sands, Appl. Phys. Lett. 52 (1988) 197.
- [6] L.-S. Hsu, Y.-K. Wang, G.Y. Guo, C.S. Lue, Phys. Rev. B 66 (2002) 205203.
- [7] L.-S. Hsu, Y.-K. Wang, G.Y. Guo, Nucl. Instrum. Methods Phys. Res. B 199 (2003) 200.

- [8] L.-S. Hsu, K.-L. Tsang, S.-C. Chung, in: L.J. Terminello, S.M. Mini, H. Ade, D.L. Perry (Eds.), Applications of Synchrotron Radiation Techniques to Materials Science III, MRS Symposia Proceedings No. 437, Materials Research Society, Pittsburgh, 1996, p. 53.
- [9] W.F. Pong, K.P. Lin, Y.K. Chang, M.-H. Tsai, H.H. Hsieh, J.Y. Pieh, P.K. Tseng, J.F. Lee, L.-S. Hsu, J. Synchrotron Rad. 6 (1999) 731.
- [10] Y.K. Chang, K.P. Lin, W.F. Pong, M.-H. Tsai, H.H. Hsieh, J.Y. Pieh, P.K. Tseng, J.F. Lee, L.-S. Hsu, J. Appl. Phys. 87 (2000) 1312.
- [11] L.-S. Hsu, A.I. Nesvizhskii, J. Phys. Chem. Solids 62 (2001) 1103.
- [12] A.N. Mansour, A. Dmitrienko, A.V. Soldatov, Phys. Rev. B 55 (1997) 15531.
- [13] L.-S. Hsu, Y.-K. Wang, G.Y. Guo, J. Appl. Phys. 92 (2002) 1419.
- [14] G.Y. Guo, Y.-K. Wang, L.-S. Hsu, J. Magn. Magn. Mater. 239 (2002) 91.
- [15] L.-S. Hsu, K.-L. Tsang, S.-C. Chung, J. Magn. Magn. Mater. 177–181 (1998) 1031.
- [16] G.Y. Guo, Y.-K. Wang, L.-S. Hsu, Phys. Rev. B 66 (2002) 054440.
- [17] D.A. Muller, S. Subramanian, P.E. Batson, S.L. Sass, J. Silcox, Phys. Rev. Lett. 75 (1995) 4744.
- [18] D.A. Muller, D.J. Singh, J. Silcox, Phys. Rev. B 57 (1998) 8181.
- [19] L.-S. Hsu, R.S. Williams, J. Phys. Chem. Solids 55 (1994) 305.
- [20] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, Techn. University Wien, Austria, 2001.
- [21] A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, Phys. Rev. B 58 (1998) 7565.
- [22] L.-S. Hsu, G.Y. Guo, C.-J. Chen, M.-D. Lan, J.-F. Lee, in: P.G. Allen, S.M. Mini, D.L. Perry, S.R. Stock (Eds.), Applications of Synchrotron Radiation Techniques to Materials Science VI, MRS Symposia Proceedings No. 678, Materials Research Society, Pittsburgh, 2001, pp. EE8.5.1–EE8.5.6.
- [23] L.-S. Hsu, Y.-K. Wang, G.Y. Guo, Y.-J. Huang, M.-D. Lan, in: V. Tikare, E.A. Olevsky, A. Zavaliangos (Eds.), Modeling and Numerical Simulation of Materials Behavior and Evolution, MRS Symposia Proceedings No. 731, Materials Research Society, Pittsburgh, 2002, pp. 301–306.
- [24] P. Horsch, W. von der Linden, W.-D. Lukas, Solid State Commun. 62 (1987) 359.
- [25] R. Weht, W.E. Pickett, Phys. Rev. B 58 (1998) 6855.
- [26] W. Pearson (Ed.), Handbook of Lattice Spacings and Structures of Metals, Pergamon, New York, 1958.
- [27] L.-S. Hsu, Y.D. Yao, Y.Y. Chen, Mod. Phys. Lett. B 11 (1997) 407.