Experimental and theoretical study of the electronic structure of Fe$_3$Al, Fe$_2$VAl, and Fe$_2$VGa

L.-S. Hsu  
Department of Physics, National Chang-Hua University of Education, Chang-Hua 50058, Taiwan, Republic of China

Y.-K. Wang and G. Y. Guo  
Department of Physics, National Taiwan University, Taipei 106, Taiwan, Republic of China  
C. S. Lue  
Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan, Republic of China

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The electronic structures of Fe$_3$Al, Fe$_2$VAl, and Fe$_2$VGa are studied by x-ray absorption near-edge spectroscopy (XANES) at the Fe and V K edges. The experimental XANES spectra are compared with those obtained from first-principles electronic-structure calculations. The experimental XANES features for these intermetallic compounds reflect the Fe- and V-p unoccupied partial density of states. The magnetic moments and the density of states at the Fermi energy at different atomic sites and spins are calculated and compared with experimental and previous theoretical values.

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I. INTRODUCTION

Intermetallic compound Fe$_3$Al crystallizes in a face-centered cubic (fcc) structure ($D_0_3$) (see Fig. 1). There are three Fe atoms per unit cell belonging to two different types. The first type consists of one Fe atom [denoted by Fe(I)] in the unit cell. It is surrounded by eight Fe atoms in an octahedral coordination. The second type consists of two Fe atoms [denoted by Fe(II)] in the unit cell. They are surrounded by four Al and four Fe atoms in a tetrahedral coordination. Fe$_3$Al has a number of unusual electronic and magnetic properties that make it attractive for high-temperature applications. It is a ferromagnetic metal with $T_c$ = 713 K and spin magnetic moment of 2.2$\mu_B$ and 1.45$\mu_B$ for the Fe(I) and Fe(II) atoms, respectively.$^1$ Its magnetic property is coupled strongly to its crystalline structure. When Fe(I) is replaced by V, the resultant structure is a Heusler-type compound (Fe$_2$VAl) with the cubic $L2_1$ lattice (see Fig. 1). Although the Fe$_2$Ga phase does not exist, the Heusler-type compound Fe$_2$VGa also crystallizes in the $L2_1$ structure. Interestingly, both Fe$_2$VAl and Fe$_2$VGa show the absence of ferromagnetic ordering.

While Fe$_3$Al has been classified as a ferromagnetic metal, semiconductinglike behavior was observed in Fe$_2$VAl and Fe$_2$VGa, as evidenced by their negative temperature coefficient of electrical resistivity.$^2,3$ Several theoretical calculations$^4-8$ predicted the presence of a pseudogap in Fe$_2$VAl, due to the hybridization effects. The pseudogap formation arises from an indirect band overlap at the Fermi energy ($E_F$), and thus Fe$_2$VAl is characterized as a semimetal. Results of nuclear magnetic resonance (NMR) measurements$^9,10$ are in good agreement with these calculations. An optical-conductivity measurement on Fe$_2$VAl further confirmed the existence of a pseudogap at $E_F$.$^{11}$ Band-structure calculations also indicated that Fe$_2$VGa is a semimetal.$^7,8$ and a recent NMR study on this material has revealed a small density of states (DOS) at $E_F$ within the pseudogap,$^{12}$ consistent with the semimetallic characteristics of this compound.

In this article, x-ray absorption near-edge spectra (XANES) at the Fe and V K edges of Fe$_3$Al, Fe$_2$VAl, and Fe$_2$VGa were measured and were compared with theoretical XANES spectra. Such analysis is especially important for establishing a relationship between the experimental XANES spectra and the unoccupied part of the local DOS and obtaining quantitative information about hole numbers and charge transfer in these intermetallic compounds. The total and site- and spin-decomposed magnetic moments and DOS’s at $E_F$ [$n(E_F)$] of these three intermetallic compounds are calculated and compared with corresponding experimental and theoretical values. This article is organized as follows. In Sec. II, the experimental and the theoretical methods are described. In Sec. III, the results and discussion are presented. The conclusions of this work are contained in Sec. IV.

![FIG. 1. Unit cell of four interpenetrating fcc sublattices showing the four types of site at Al (Ga) (000), B ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), C ($\frac{1}{2}, \frac{1}{2}, 0$), and D ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$). Structures: $D_0_3$ Fe$_3$Al, $B$ = Fe(I), $C$ = $D$ = Fe(II); $L2_1$ Fe$_2$VAl, and Fe$_2$VGa, $B$ = V, $C$ = $D$ = Fe.](image)
The resulting Fe$_2$V Al ingot was annealed in a vacuum-sealed crucible and then melting several times in an Ar arc furnace. High-purity elemental metals in a water-cooled copper crucible for polycrystals were prepared by mixing appropriate amounts of these pure elements, followed by annealing at 1000°C for two days, and then melting several times in an Ar arc furnace. The resulting Fe$_2$V Al ingot was annealed in a vacuum-sealed (10$^{-5}$ Torr) quartz tube at 1000°C for two days, and then at 400°C for 12 h. The Fe$_2$Ga ingot was annealed at 600°C and then 400°C for 24 h. They were then furnace-cooled to room temperature. The same preparation techniques have been used in other studies of these two materials, which are known to form in a single-phase L2$_1$ Heusler-type structure. X-ray diffraction patterns were carried out with the Cu $K\alpha$ radiation on powdered substances, and the expected L2$_1$ structure was observed for Fe$_2$VAl and Fe$_2$Ga. The lattice constants were determined to be 5.76 and 5.77 Å for Fe$_2$VAl and Fe$_2$Ga, respectively. These values are essentially the same as those reported in the literature. Wavelength dispersive spectroscopy showed that these two compounds are uniform in composition. No signs of a second phase were seen in the second phase in these materials.

The XANES experiments were carried out on beam lines 17C and 15B at the Synchrotron Radiation Research Center, Taiwan. A Si(111) double-crystal monochromator was used and the typical energy resolution was about 1 eV. The XANES spectra were collected by recording the total yield of secondary electrons from the sample surfaces at room temperature. Standard 5-μm-thick Fe and V foils were used as references for energy calibration. 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.

B. Theoretical methods

In order to calculate the theoretical XANES spectra and other physical parameters of Fe$_2$Al, Fe$_2$VAl, and Fe$_2$VGa, we use the highly accurate all-electron full-potential linear augmented-plane-wave (FLAPW) method. The calculations are based on the first-principles density-functional theory with the generalized gradient approximation (GGA) to the exchange-correlation potential. We begin the calculations by determining the total energies at several values of the lattice constants near the experimental ones. These energies are then fitted to the Murnaghan equation of state to obtain the theoretical equilibrium lattice constants and bulk moduli. The theoretical and experimental lattice constants of these three compounds are shown in the fourth column in Table I. We note that previous authors used local spin-density approximation (LSDA) to calculate the electronic structures of Fe$_2$Al and Fe$_2$VAl. We thus also used LSDA to calculate the theoretical equilibrium lattice constants of Fe$_2$VAl (5.95 Å) and Fe$_2$VGa (5.99 Å). Obviously, these two values differ more from the respective experimental values than those calculated with the GGA method (see Table I). Thus, GGA seems more accurate than LSDA in calculating the electronic structures of these compounds, and we will use it in all the calculations. The muffin-tin radius of 1.27 and 1.22 Å is used for V and Al(Ga) atoms, respectively. The wave functions, the charge densities, and the potentials are expanded in terms of spherical harmonics inside the muffin-tin spheres. The cutoff angular momentum ($l_{\text{max}}$) is ten for the wave functions and six for the charge densities and the potentials. The Brillouin zone (BZ) integration is carried out by using the improved tetrahedron method. The number of the augmented plane waves included is 96 per formula unit. Thus, GGA seems more accurate than LSDA in calculating the electronic structures of these compounds, and we will use it in all the calculations. The number of the augmented plane waves included is 96 per atom, i.e., $R_{\text{m}}K_{\text{max}}=9$. The number of the $k$ points in the irreducible BZ wedge (IBZW) used in the self-consistent calculations is 47. To calculate the DOS curves and the theoretical XANES spectra, 286 k points in the IBZW were used. We have checked the convergence of the calculated eigenvalues with respect to the number of augmented plane waves used and the number of $k$ points used.

III. RESULTS AND DISCUSSIONS

The calculated total energy of the ferromagnetic Fe$_2$Al phase is lower than that of the paramagnetic one by 1.13 eV per formula unit. Thus, the XANES spectrum obtained from the spin-polarized calculation of Fe$_2$Al is used to compare with the experimental spectrum. On the other hand, since Fe$_2$VAl and Fe$_2$VGa are nonmagnetic, the theoretical XANES spectra of the paramagnetic state are used for comparing with the experimental XANES spectra. We did perform the spin-polarized calculations of Fe$_2$VAl and Fe$_2$VGa,
and, indeed, no difference from those of the non-spin-polarized calculations was found. The experimental (open circles) and theoretical (solid line) Fe K-edge XANES spectra for Fe$_3$Al, Fe$_2$VAI, and Fe$_2$VGa, respectively. Also shown are the Fe $p$ partial DOS curves (dots).

The maxima of the experimental XANES spectra in Figs. 2 and 3, which correspond to Fe and V $1s$ to $ep$ transitions, coincide with the peaks in the Fe and V $p$ partial DOS curves, respectively. The zero energy in Figs. 2 and 3 corresponds to the inflection points of the Fe and V K-edge absorption thresholds (7112.5 and 5455 eV, respectively). The experimental data were normalized to the theoretical spectra in the region 10–20 eV above the absorption edges. Overall, we have a reasonably good agreement between theoretical and experimental results. The white-line positions and intensities and the absorption peaks above the white-line energies are well reproduced in the theoretical spectra. Small 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 is that the GGA eigenvalues are not the true excitations of the XANES spectra, and errors 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 is that the GGA eigenvalues are not the true excitations of the XANES spectra, and the errors in peak positions are comparable to the self-energy correction between GGA and more sophisticated methods such as GW. 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 calculations. As for the source of the discrepancy in peak width, the

FIG. 2. (a)–(c). The experimental (open circles) and theoretical (solid line) Fe K-edge XANES spectra for Fe$_3$Al, Fe$_2$VAI, and Fe$_2$VGa, respectively. Also shown are the Fe $p$ partial DOS curves (dots).

XANES spectra of V K-edge and V $p$ partial DOS for Fe$_2$VAI and Fe$_2$VGa are depicted in Figs. 3(a) and 3(b), respectively. The zero energy in Figs. 2 and 3 corresponds to the inflection points of the Fe and V K-edge absorption thresholds (7112.5 and 5455 eV, respectively). The experimental data were normalized to the theoretical spectra in the region 10–20 eV above the absorption edges. Overall, we have a reasonably good agreement between theoretical and experimental results. The white-line positions and intensities and the absorption peaks above the white-line energies are well reproduced in the theoretical spectra. Small 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 is that the GGA eigenvalues are not the true excitations of the XANES spectra, and errors in peak positions are comparable to the self-energy correction between GGA and more sophisticated methods such as GW. 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 calculations. As for the source of the discrepancy in peak width, the

FIG. 3. (a) and (b). Same as in Fig. 2, except for V K-edge and V $p$ partial DOS for Fe$_2$VAI and Fe$_2$VGa, respectively.
hot-electron lifetime is strongly energy dependent so that it mostly damps peaks about 20 eV above the absorption edge.

The calculated and experimental total $n(E_F)$ values for Fe$_3$Al, Fe$_2$VAl, and Fe$_2$VGa are listed in the fifth column in Table I, and the site- and spin-decomposed $n(E_F)$ values are listed in Table II. Also included in Table II are those values for Fe metal. The total $n(E_F)$ value for ferromagnetic Fe$_3$Al is 2.78 states/eV cell, which yields the electron-phonon mass enhancement factor of 0.11 when compared with the experimental value (3.09 states/eV cell)$^{21}$ of DO$_3$Fe$_2$Al obtained from specific-heat measurement. We note that the experimental $n(E_F)$ value for Fe$_3$Al could increase by a maximum of 20% from the above-sited value when the sample was heat treated. $^{21}$ This is because various heat treatment of Fe$_3$Al changes the local atomic environment of the Fe atoms to form different phases. $^{22}$ The ferromagnetic $n(E_F)$ value for Fe$_3$Al in Table I is essentially the same as that (2.75 states/eV cell)$^4$ obtained from a previous self-consistent calculation and is much smaller than the earlier non-self-consistently calculated value (5.79 states/eV cell)$^{23}$ of DO$_3$Fe$_2$Al obtained from specific-heat measurement. From Table II, one can see that the spin-up and spin-down $n(E_F)$ values of Fe(I) atoms in Fe$_3$Al are close to those of the Fe metal, but the $n(E_F)$ value of the spin-down Fe(II) atoms in Fe$_3$Al is considerably larger than $n(E_F)$ values of the Fe metal. This implies that the contribution to the total $n(E_F)$ value for Fe$_3$Al is dominated by the spin-down Fe(II) 3$d$ electrons, which was confirmed by earlier electrical-resistivity study.$^{24}$ The calculated $n(E_F)$ values for Fe$_2$VAl and Fe$_2$VGa are 0.18 and 0.28 states/eV cell, respectively, and the major contribution to the higher $n(E_F)$ value for Fe$_2$VGa comes from that of the V sites in this compound, as can be seen in Table II. The V partial $d$-spin contributions to the $n(E_F)$ values for Fe$_2$VAl (Ref. 10) and Fe$_2$VGa (Ref. 12) are 0.023 and 0.085 states/eV cell, respectively, as derived from the NMR studies on these two compounds. Our theoretical values (0.062 and 0.128 states/eV cell for Fe$_2$VAl and Fe$_2$VGa, respectively) are larger than these two experimental ones. On the other hand, our calculated total $n(E_F)$ value for Fe$_2$VAl is essentially the same as that calculated previously (0.1 states/eV cell).$^5$ We note that the theoretical and NMR-derived $n(E_F)$ values for Fe$_2$VAl and Fe$_2$VGa are considerably larger than the experimental ones obtained from specific-heat measurements.$^{14}$

The calculated paramagnetic and ferromagnetic values of the bulk modulus ($B$) for Fe$_3$Al are 2.04 and 1.67 Mbar, respectively, and are listed in the last column in Table I. The previously reported theoretical $B$ values [1.59 (Ref. 22) and 1.83 (Ref. 25) Mbar] for Fe$_3$Al are close to our ferromagnetic $B$ value. The calculated $B$ values for Fe, Fe$_2$VAl, and Fe$_2$VGa are 1.85, 2.12, and 2.14 Mbar, respectively. To our knowledge, there are no experimental $B$ values reported for Fe$_3$Al, Fe$_2$VAl, and Fe$_2$VGa.

In Table II, the calculated site-projected and total magnetic moments ($M_s$) are listed in the first row for Fe and Fe$_2$Al. For Fe$_3$Al, the $M_s$ value is 2.51 $\mu_B$/atom for the Fe atoms on sites with eight Fe nearest neighbors [Fe(I) atoms], 1.96 $\mu_B$/atom for the other Fe atoms on sites with four Fe and four Al nearest neighbors [Fe(II) atoms], and $-0.12$ $\mu_B$/atom for the Al atoms. These values are close to those reported previously by other theorists (2.4, 1.8, and $-0.13$ $\mu_B$/atom, respectively)$^{25}$ and experimentalists (2.2 and 1.45 $\mu_B$/atom, respectively, for Fe(I) and Fe(II) atoms)$^{21}$.

Earlier experimentalists,$^{26}$ using neutron-diffraction measurement, reported similar $M_s$ values for Fe$_3$Al at the Fe(I) (2.18 $\mu_B$/atom) and Fe(II) (1.50 $\mu_B$/atom) atomic sites. However, the $M_s$ values (2.16 and 1.26 $\mu_B$/atom, respectively) obtained from a non-self-consistent calculation$^{23}$ are smaller than those obtained from present self-consistent calculation. We should mention that, in Table II, the Fe(I) atoms in Fe$_3$Al possess nearly the same $M_s$ value as Fe atoms in bcc Fe metal, which also have eight Fe nearest neighbors. This observation was confirmed by neutron-diffraction study.$^{27}$ On the other hand, the difference between the $M_s$ values of the Fe(II) atoms in Fe$_3$Al and of the Fe atoms in Fe metal is attributed to the increase of DOS near the top of the spin-down Fe 3$d$ band in Fe$_3$Al. Thus, the Fe moment in Fe and Fe$_3$Al is only a function of the number of nearest Fe neighbors. The total $M_s$ value for Fe$_3$Al is 6.10 $\mu_B$/atom, which is close to the experimental values of 5.61 $\mu_B$/atom.$^{28}$

The number of Fe 3$d$ electrons calculated for Fe$_3$Al is 6.25, which is close to the value (6.59) reported previously.$^{29}$ The number of Fe 3$d$ electrons for Fe metal calculated in this work is 6.15. The number of Fe 3$d$ electrons calculated for Fe$_2$VAl and Fe$_2$VGa is 6.25 and 6.26, respectively; while that for V 3$d$ electrons is 2.98 and 2.99, respectively. The constancy in Fe 3$d$ electrons between Fe metal and these three intermetallic compounds is also observed in a lot of other metallic alloys.$^{29}$

<table>
<thead>
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<th>Material</th>
<th>Fe(I)</th>
<th>Fe(II)</th>
<th>V</th>
<th>Al (Ga)</th>
<th>interstitial</th>
<th>total</th>
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</thead>
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<tr>
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<td></td>
<td>0.82</td>
<td>-0.07</td>
<td>2.38</td>
<td></td>
</tr>
<tr>
<td>Fe$_3$Al</td>
<td>2.51</td>
<td>1.96</td>
<td>-0.12</td>
<td>-0.21</td>
<td>6.10</td>
<td></td>
</tr>
<tr>
<td>Fe$_2$VAl</td>
<td>0.096</td>
<td>0.062</td>
<td>0.007</td>
<td>0.017</td>
<td>0.18</td>
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<td>0.128</td>
<td>0.008</td>
<td>0.024</td>
<td>0.28</td>
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</tr>
</tbody>
</table>
IV. CONCLUSIONS

The electronic structures of Fe$_3$Al, Fe$_2$VAl, and Fe$_2$VGa are studied jointly by XANES measurements at the Fe and V K edges and by theoretical analysis using FLAPW method. A reasonably good agreement between theory and experiment is found. The experimental XANES features for these compounds reflect the Fe- and V-$p$ unoccupied density of states. The magnetic moments and the density of states at the Fermi energy at different atomic sites and spins are calculated and compared with experimental and other theoretical values.

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