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Abstract
X-ray and soft x-ray photoelectron spectra were taken on Fe2VAl samples. The Fe–3s spectra show a shoulder on the higher binding energy side of the main peak, split by ≈4.7 eV. Based on current understanding of core-level multiplet splitting in transition-metal compounds, we believe this is direct evidence of a local moment in Fe2VAl.

Keywords
Ames Laboratory, photoelectron spectra, multiplet splitting

Disciplines
Atomic, Molecular and Optical Physics | Condensed Matter Physics | Physics

Comments
Fe-3s core-level splitting and local magnetism in Fe$_2$VAI

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X-ray and soft x-ray photoelectron spectra were taken on Fe$_2$VAI samples. The Fe-3s spectra show a shoulder on the higher binding energy side of the main peak, split by ~4.7 eV. Based on current understanding of core-level multiplet splitting in transition-metal compounds, we believe this is direct evidence of a local moment in Fe$_2$VAI.

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I. INTRODUCTION

Fe$_2$VAI was shown recently to have fascinating physical properties. With an enhanced density of states at $E_F$ seen in photoemission and specific-heat measurements, and the negative temperature coefficient of its unusually large resistivity, heavy fermion physics was proposed. There is also evidence contradictory to the ground state of a Kondo lattice. First, 3$d$ electrons are more delocalized than their 4$f$ counterparts. Significant overlap of the wave functions tends to suppress the Kondo effect, making 3$d$ counterparts. Significant overlap of the wave function tends to reveal the physics behind Fe$_2$VAI.

The valence band of Fe$_2$VAI has since been investigated through x-ray and soft x-ray photoelectron spectroscopy. The shallow-core-level multiplet splitting and local magnetism in Fe$_2$VAI represent a diagnostic tool for local moments. However, calculations using Hartree-Fock theory, based on the one-electron approximation, yielded too large a splitting and a different intensity ratio, compared to experiments. Bagus, Freeman, and Sasaki were the first to realize that intra-atomic configuration interaction of the electrons within the same subshell, largely due to the near degeneracy of the orbital energies of the $3p^2$ and $3s3d$ configurations, causes a significant modification to the final states. By including additional internal configurations, they were able to account for both the size of the 3s splitting and the intensity ratio of the Mn$^{2+}$ compound.

The success in understanding Mn$^{2+}$ multiplet splittings lies in the half-filled 3$d$ shell. Local screening is suppressed due to a large ligand-to-3$d$ charge-transfer gap. Aside from magnetic insulators with Mn$^{2+}$ ions, however, the relation between 3$s$ splitting and the local magnetic moment is not as straightforward. Studies have found that for many metals, metalloids, and nonmetals containing Fe, the splitting of 3$s$ levels is not proportional to the local moment measured by neutron scattering, saturation magnetization, or hyperfine fields. In two references, the Anderson Hamiltonian in the impurity approximation was solved, treating exchange splitting, intra-atomic degeneracy, and screening by ligands on an equal footing. In both accounts, screening was found to be an integral part of XPS spectra. With increasing atomic number of cations (from Mn) or decreasing electronegativity of ligands, the charge-transfer energy from ligand to 3$d$ atom becomes smaller; thereby local screening by the charge-transferred 3$d$ electron becomes more likely. A direct extraction of exchange energy from the splitting of the two strongest peaks, without regard to local screening, is unwarranted. Experimentally, if the charge-transfer satellite of the 2$p$ core level is small, the major multiplet splitting of 3$s$ is still a good measure of the exchange energy, with the intrashell...
redistribution of electrons only contributing to satellites at much higher energy. 18,24

Recent advances in high-resolution spin-polarized photoemission have made more detailed experiments possible. In separate efforts, three groups 25–27 have measured the $3s$ splitting of Fe metal. One single peak dominates minority-spin emission at the lower binding energy but two structures were discovered in the majority-spin emission 0.9 and 4.5 eV higher in binding energy. Although the theoretical modeling 28 of Fe, based on the atomic Fe $3d^7$ ion, gave a fair estimate of the energy separation of the high- and low-spin final states and also the relative intensities, the origin of the 0.9-eV difference between majority and minority emissions of the high-spin component is still elusive. It is prudent to say that within current understanding, exchange splitting is the cause of the satellite of Fe-$3s$ core level, 4.5 eV below the main peak.

In this work we report the observation of Fe-$3s$ satellite structures in the Heusler-like alloy Fe$_2$VAl. In conjunction with recent understanding of the multiplet splitting, we propose that this final-state structure is the first signature of local magnetic moments in Fe$_2$VAl.

II. EXPERIMENTS

The samples involved were grown by the Bridgman method (sample B2), Czochralski method (sample C), and arc melting (samples A1 and A2). Their growth procedure, chemical composition, crystal structure, and magnetic and transport properties were described in another paper. 6 It suffices to point out here that most samples are close to stoichiometric Fe$_2$VAl with various degrees of Fe and Al deficiency, except for $C$, which is Fe rich. Severe antise structural disorder was found in all samples by x-ray diffraction. Saturation magnetization measurements at 2 K found at least two kinds of superparamagnetic clusters in samples A2 and B2. A1 and $C$ were found to have magnetic transitions around 18 K and 50 K, respectively.

The XPS spectra at room temperature were taken using a Physical-Electronics 5500 Multi-Technique system with monochromatized Al $K_α$ radiation. A hemispherical electron energy analyzer was used. The resolution of the spectrometer (FWHM) was 0.65 eV, with a spot size around 1 mm $\times$ 1 mm. The base pressure of the XPS system was less than $7 \times 10^{-10}$ Torr, and $4 \times 10^{-10}$ Torr in the preparation chamber. We have also taken spectra using 150-eV synchrotron radiation at the Synchrotron Radiation Center. With a slit width of 70 $\mu$m on a 2-m ERG monochromator and pass energy of the electron analyzer of 50 eV, a comparable resolution was achieved at the Ames-Montana beamline. Pressure of this UHV system is $5 \times 10^{-11}$ Torr.

The XPS data-analysis package was used to obtain the atomic concentrations. Corrections due to the photoionization cross section of atomic shells, electron escape depth, transmission function of the electron analyzer, and detection angle had been applied. The atomic percentage, obtained by integrating C-$1s$, O-$1s$, Al-$2p$, V-$2p$, and Fe-$2p$ photoelectrons.

Fracturing the samples in situ is found to yield surfaces with least oxygen and carbon content. Using inert gas etching or in-situ grinding to clean sample surfaces were not proper procedures. During argon-ion bombardment preferential sputtering of the lightest element (Al) was observed. After grinding with a diamond wheel several times, large amounts of oxide and carbon remained on the surface. We chose to break the samples in situ. There was always 5 at. % oxygen contamination right after fresh surfaces of Fe$_2$VAl were uncovered. When these surfaces were further exposed to oxygen, aluminum oxide quickly formed to become the major oxide on the surface. Even with vacuum as good as $5 \times 10^{-11}$ Torr, aluminum oxide showed up as a distinct shoulder in the Al-$2p$ spectrum 24 h after cleavage. Intensive argon-ion sputtering of the fractured surface of sample A2 yielded about 3 at. % oxygen remaining. Fe and V oxide formation as evidenced by the change of slope at the higher-
binding energy side of the 2p peaks were less obvious and were detected only after aluminum oxide peaks were evident. Surface carbon content right after cleaving was less than 4 at. % for all samples except A2, which had almost 9 at. %. We found regularly two peaks associated with the carbon 1s orbital. The one with binding energy near 285 eV changed with surface conditions. Associated with the C–H bond, this peak diminished to zero with sputtering but regained its intensity after time in vacuum. The other peak at 283-eV binding energy was identified to be from carbide bonding. This carbide peak gained some intensity in the middle of the sputtering, similar to the carbide formation on the TiFe surface activated by ion bombardment.29 Terminal carbon intensity in sample A2 is around 3 at. %. Carbon concentration at this level was found to bear no relation to the core-level spectra of any other element. Still, the carbon and aluminum (oxide) peaks were checked during the integration of the Fe-2p and Fe-3s data to insure that there was no detectable contamination. All spectra discussed in the following were taken right after cleavage, without sputtering and before aluminum oxide appeared. The composition of Fe, V, and Al on these surfaces was compared to the stoichiometries measured by atomic emission spectroscopy.6 The relative atomic ratios are consistent with each other. Therefore, the electronic and magnetic properties of the in-situ fractured surfaces are regarded to be representative of the bulk.

III. RESULTS AND DISCUSSION

Fe-2p and Fe-3s spectra of all Fe2VAl samples, together with that of pure Fe, are shown in Figs. 1 and 2. The Fe-3p spectrum of sample A2 was taken at 150-eV photon energy with better vacuum, and that of pure Fe was taken...
TABLE I. Comparison of line-shape parameters of Fe-3s spectra and magnetic moments in Fe$_2$VAl and pure Fe. $\gamma_1$ and $\gamma_2$ are the Lorentzian widths of the main and satellite peaks. $\alpha_s$ is the asymmetry parameter of the DS line shape of the main peak. $\alpha_s = 0$ in all fittings. $I_1/I_2$ is ratio of integrated intensities. $\mu$ is the saturation moment measured at 2 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta E$ (eV)</th>
<th>$\gamma_1$ (eV)</th>
<th>$\gamma_2$ (eV)</th>
<th>$\alpha_1$</th>
<th>$I_1/I_2$</th>
<th>$\mu$ ($\mu_B$/f.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathcal{B}2$</td>
<td>4.7</td>
<td>1.27</td>
<td>2.0</td>
<td>0.13</td>
<td>5.4</td>
<td>0.05</td>
</tr>
<tr>
<td>$\mathcal{C}$</td>
<td>4.7</td>
<td>1.23</td>
<td>2.3</td>
<td>0.13</td>
<td>5.4</td>
<td>0.33</td>
</tr>
<tr>
<td>$\mathcal{A}1$</td>
<td>4.6</td>
<td>1.27±0.03</td>
<td>2.3±0.3</td>
<td>0.10±0.02</td>
<td>4.1</td>
<td>0.37</td>
</tr>
<tr>
<td>$\mathcal{A}2$</td>
<td>4.6</td>
<td>1.25</td>
<td>2.3</td>
<td>0.13</td>
<td>5.1</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe</td>
<td>4.9±0.3</td>
<td>1.20±0.03</td>
<td>3.4±0.3</td>
<td>0.15±0.02</td>
<td>2.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Fe$^{30b}$</td>
<td>4.8</td>
<td>0.19</td>
<td>1.1</td>
<td>1.3-1.8</td>
<td>0.27</td>
<td>4.5</td>
</tr>
<tr>
<td>Fe$^{20c}$</td>
<td>4.9</td>
<td>1</td>
<td>1.3</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Standard deviation of our fitting, unless otherwise indicated.  
$^b$Mg $K_a$ used; linear background subtraction; $\alpha_2 = 0.08$.  
$^c\alpha_1 = \alpha_2$ forced; no background corrections.

with Al $K\alpha$ excitation. They are shown in Fig. 3. All spectra have been normalized to a peak intensity of 100 and displaced relatively for ease of viewing. With only one spin-orbit doublet, none of the Fe-2$p$ spectra has extra peaks due to chemical shifts or plasmon excitations. Without any satellite structure in the 2$p$ or 3$p$ spectra, we can also rule out the importance of local screening. The lesser asymmetry of Fe$_2$VAl peaks, relative to that of Fe, observed in all core levels hints at the suppressed electron-hole pair excitations near $E_F$ in Fe$_2$VAl samples. All 3$s$ spectra have shoulders around 5 eV below the main peak.

In the case of Fe, spin-polarized photoemission 25–27 reveals the existence of three peaks. With our experimental resolution comparable to the smallest separation of these peaks, we cannot fit all three peaks and perform line-shape analysis. However, we can still compare Fe$_2$VAl with Fe, in the spirit of Refs. 20 and 30. For each 3$s$ spectrum, a Shirley background 31 was subtracted first and the remainder was fit with two peaks of Doniach-Šunjić (DS) line-shape. The standard deviations of each parameter were obtained in the least-square Marquardt-Levenberg fitting. Relevant parameters of this fitting and selected literature results are given in Table I. The difference between our fitting results and those of Ref. 20 for pure Fe is primarily due to the Shirley background subtraction and the independence of $\alpha_1$ and $\alpha_2$ in our fitting. Although the asymmetry parameter $\alpha$ depends on the shape of the density of states near $E_F$ and would allow us to obtain more information, 32 it was recognized that the interference of the nearby majority-spin emission alters the apparent $\alpha$ of the main peak. 26 $I_1/I_2$ is strongly affected also.

As shown in Table I, all Fe-3$s$ splitting parameters are very similar, although the saturation moment varies by an order of magnitude. All samples show a secondary peak with considerable intensity 4.7 eV below the main peak. This is very similar to the case of pure Fe. Assuming the proportionality of exchange splitting and 2$S+1$ still applies, this secondary peak provides evidence that a large fraction of the Fe atoms in Fe$_2$VAl carry a local moment of around 2.2$\mu_B$. Singh and Mazin 8 found that although Fe$_2$VAl in the ordered $L_2_1$ phase will have no moment on the Fe atoms, the local moment on antisite Fe atoms is very robust, always 2.2–2.3$\mu_B$. These XPS spectra therefore confirm the large amount of antisite structural disorder found in Fe$_2$VAl. 6 The small saturation moments at low temperature do not necessarily contradict the large relative intensity of the satellite.

Our study of Fe$_2$VAl (Ref. 6) has found not only two types of superparamagnetic clusters composed of magnetic antisite Fe atoms, but more antisite Fe atoms that are probably locked in a spin-glass state. The Fe atoms in superparamagnetic clusters give a small saturation moment of 0.02–0.37$\mu_B$/f.u. at 2 K, probably even less at elevated temperatures. However, all antisite Fe atoms, including those in the spin-glass state, should carry a local moment and contribute to the intensity of the satellite.

In summary, our Fe-3$s$ spectra show that a large number of Fe atoms in Fe$_2$VAl are in antisite disorder. Each one carries a moment of 2.2$\mu_B$. Further spin-polarized photoelectron experiments should clarify the details.

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