

High-resolution photoelectron spectroscopy of Heusler-type Fe₂VAl alloy†

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The electronic structure of Heusler-type Fe₂VAl has been studied by high-resolution photoelectron spectroscopy with the excitation photon energy $h\nu$ ranging from 21.2 eV (the He I laboratory light source) to 904 eV (the soft X-ray synchrotron light source) for clean surfaces prepared by scraping or fracturing polycrystalline and single crystalline specimens. Photoelectron spectra recorded for the fractured surfaces show a 10 eV-wide valence band with fine structures and a clear decrease in the intensity towards the Fermi level E_F , while a high intensity at E_F and no fine structures are observed for the scraped surface. Comparison with the theoretical density of states (DOS) indicates that the vacuum ultraviolet photoelectron spectra emphasize the transition-metal 3d bands but the soft X-ray photoelectron spectra agree remarkably well with the DOS including the fine structures and the pseudogap at E_F . The present results suggest that the electronic structure of Fe₂VAl is highly sensitive to possible strain and defects induced by scraping. Bulk electronic structures of Fe₂VAl are discussed in relation to the reported fascinating transport properties.

Keywords: Heusler-type Fe₂VAl; electronic structure; pseudogaps; high-resolution photoelectron spectroscopy; ultraviolet photoelectron spectroscopy; UPS; soft X-ray photoelectron spectroscopy; XPS.

1. Introduction

The Heusler-type intermetallic compound Fe₂VAl has attracted special attention because of its fascinating physical properties. This compound is found to be in a marginally magnetic state between ferromagnetic and non-magnetic or paramagnetic states (Kato *et al.*, 2000) and shows unusual transport properties, *i.e.* a semiconductor-like behaviour of electronic conductivity over a wide temperature range between 2 K and 1200 K with a value reaching 30 $\mu\Omega$ m at 2 K and an effective electron mass enhancement at low temperatures

(Nishino *et al.*, 1997; Kato *et al.*, 2000). These facts are reminiscent of the heavy fermion system. The resistivity in the temperature range between 400 K and 800 K suggests an energy gap of about 0.1 eV, although its temperature dependence cannot be explained in terms of a single band-gap picture (Nishino *et al.*, 1997). On the other hand, several band calculations consistently predict that Fe₂VAl is a non-magnetic semi-metal with a pronounced pseudogap of 0.5 eV right at the Fermi level E_F (Guo *et al.*, 1998; Singh & Mazin, 1998; Weht & Pickett, 1998; Weinert & Watson, 1998; Bansil *et al.*, 1999; Botton *et al.*, 2000). A nuclear magnetic resonance study reveals a semi-conducting gap of 0.27 eV at high temperatures and a small density of carriers (Lue & Ross, 1998). Optical conductivity data for Fe₂VAl also indicate a 0.2 eV-wide optical gap with a small Drude-like contribution (Okamura *et al.*, 2000), which is consistent with the results of the Hall coefficient measurement (Kato *et al.*, 1998). Very recently it has been found that a small deviation of the Al content from stoichiometry results in a large enhancement of the Seebeck coefficient (thermoelectric power) with a change in its sign, which may also imply the existence of a pseudogap across E_F (Nishino *et al.*, 2001).

In order to clarify the mechanism of the unusual transport properties of Fe₂VAl, it is important to understand its electronic structure experimentally by photoelectron spectroscopy. In spite of the above-mentioned implication of a pseudogap, a clear Fermi edge with large intensity was observed in the photoelectron spectrum recorded for clean surfaces prepared by scraping the specimen with a diamond file at an excitation photon energy $h\nu$ of 63 eV (Nishino *et al.*, 1997; Soda *et al.*, 1999), where the transition-metal 3d states may be emphasized (Yeh & Lindau, 1985) and the surface effect might become prominent because of the small escape depth of the photoelectrons (Zangwill, 1988a). Indeed, recent investigations have suggested that the electronic structure of Fe₂VAl may be strongly affected by a small deviation of the chemical composition and defects such as the anti-site defect (Sumi *et al.*, 2001; Maksimov *et al.*, 2001; Yoshimoto *et al.*, 2001; Deniszczyk, 2001; Nishigori *et al.*, 2000; Matsushita & Yamada, 1999). Here, the anti-site defect is an Fe atom occupying the nominal V site in the Heusler structure of Fe₂VAl and is considered to form a magnetic cluster (Singh & Mazin, 1998; Kato *et al.*, 2000). Sekiyama *et al.* (2000) have also shown the importance of probing the bulk electronic structure of materials with a strong electron correlation by high-resolution soft X-ray photoelectron spectroscopy (HRSXPS). They have found that the bulk electronic states of Ce-based Kondo materials are quite different from their surface states in hybridization and have observed the clear difference expected in the bulk electronic structures of CeRu₂ and CeRu₂Si₂, which could not be resolved without the HRSXPS.

In this paper we will report the high-resolution photoelectron spectra of Fe₂VAl recorded with various surface preparations and excitation photon energies and clarify its bulk electronic structure.

2. Experimental

The polycrystalline specimens of the Heusler-type Fe₂VAl alloy were prepared by repeated arc-melting of appropriate mixtures of 99.99% pure Fe and Al and 99.9% pure V in an argon atmosphere and subsequent homogenization at 1273 K for more than 170 ks in a vacuum (Kato *et al.*, 2000; Nishino *et al.*, 2001). After shaping the specimens into a size of 2 × 2 × 5 mm, they were annealed at 1273 K for 3.6 ks and at 673 K for 14.4 ks for the L₂₁ ordering followed by furnace cooling. Single crystalline specimens of length 5 mm and diameter 1 mm were prepared by the Czochralsky pulling method in a tetra-arc furnace under an Ar atmosphere. The chemical compo-

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sition was determined within an accuracy of ± 0.2 at% by inductively coupled argon plasma atomic emission spectroscopy or by electron probe microanalysis.

The soft X-ray photoelectron (SXPS) measurement was carried out for the polycrystalline specimens at the experimental station for high-resolution photoelectron spectroscopy of beamline BL25SU of the 8 GeV electron storage ring of SPring-8 at the Japan Synchrotron Radiation Research Institute. The spectra were recorded at 20 K with 0.10 eV total energy resolution including thermal broadening at $h\nu = 904.0$ eV by use of highly monochromatic soft X-rays from a twin helical undulator and a high-resolution hemispherical analyzer (SCIENTA SES200) (Saitoh *et al.*, 2001; Sekiyama *et al.*, 2000).

The ultraviolet photoelectron (UPS) experiment was also performed for the single crystalline specimens at the Institute for Solid State Physics, University of Tokyo, Japan, with a high-resolution photoelectron energy analyzer (GAMMADATA SCIENTA SES2002) and a He I laboratory light source (GAMMADATA VUV5000) with a toroidal grating monochromator (Yokoya *et al.*, 2000). The UPS spectra were measured at 6 K with a total energy resolution of 0.004 eV.

The angle acceptances of these analyzers were set to about $\pm 8^\circ$. The origin of the binding energy and total energy resolution were determined from the Fermi edge of Au films or Au plates placed near the specimen on a sample holder. The base pressure was 4×10^{-8} Pa for the SXPS measurement and 5×10^{-9} Pa for the UPS measurement. Clean surfaces for the photoelectron measurement were obtained by scraping the specimen with a diamond file or fracturing it with a knife edge at low temperatures. Since the single Fe₂VAl crystals were grown along the [111] direction, the fractured surface of the single crystalline specimen was supposed to be the (111) surface. Clean surfaces for the SXPS measurement were checked by measuring SXPS spectra in a wide energy range scan or in the energy region of the O 1s and V 2p lines. These SXPS spectra indicate no carbon and oxygen contamination just after the surface preparation and a very small evolution of the O 1s line in 4 h. No change in the spectral shape of the valence band was recognized during the UPS and SXPS measurements.

3. Results and discussion

Fig. 1 summarizes typical valence band photoelectron spectra of Fe₂VAl measured for the scraped and fractured surfaces with $h\nu = 21.2$ and 904.0 eV, together with the spectrum previously recorded for the scraped surface at 63 eV photoexcitation (Soda *et al.*, 1999) and one of the theoretically predicted total densities of states (Botton *et al.*, 2000). Here, the spectral intensities are normalized at their maxima. As may be clearly seen in the figure, the photoelectron spectrum recorded with an excitation photon energy of 904.0 eV for the fractured surface of the polycrystalline specimen shows a 10 eV-wide valence band with fine structures and a clear decrease in the intensity towards the Fermi level E_F . The UPS spectrum for the fractured single crystalline specimen also reveals the intensity reduction toward E_F and prominent peaks at the binding energies E_B of about 0.4 and 1.4 eV, but a fairly narrow (about 2 eV-wide) valence band spectrum. In contrast with the fractured surface a high intensity at E_F is observed, and the fine structures are smeared out for the scraped surface not only on the lower photon energy excitation but also on the 904 eV photoexcitation. Although the UPS spectra for the scraped surfaces of both the single crystalline and polycrystalline specimens are not shown here, they also show the high intensity at E_F and no prominent peaks.

The spectral features observed for the fractured surface on the 904 eV photoexcitation agree remarkably well with the theoretical DOS and indicate the existence of the predicted pseudogap. This good agreement can be ascribed to (i) comparable photoionization cross sections for various subshells consisting of the valence band at $h\nu \simeq 900$ eV, (ii) the higher bulk sensitivity of the SXPS, and (iii) the less degradation of the surface-layer structure induced by the fracture than the scraping.

According to the theoretical calculations (Guo *et al.*, 1998; Singh & Mazin, 1998; Weht & Pickett, 1998; Bansil *et al.*, 1999), the Fe 3d dominant bands hybridized with Al 3p and V 3d orbitals spread over from E_F to 5.5 eV. The band above 0.8 eV is dominated by the Fe 3d t_{2g} states, while the Al 3p states are dominant below 3.5 eV and the V 3d t_{2g} states lie mainly from 1.2 to 2.2 eV. The lowest split-off band between 5.9 and 9.3 eV is of Al 3s character strongly hybridized with Fe and V 4s states. As shown in Fig. 2, the photoionization cross sections of the Fe and V 3d electrons predominate over the other valence electrons by about one order of magnitude in the lower photon energy region, while those of the Al 3s and Fe and V 4s electrons become comparable within a factor of about three with the 3d electrons around $h\nu = 900$ eV (Yeh & Lindau, 1985). Thus the band derived from bands other than the transition-metal 3d states, such as the Al 3s-derived band, appears in the SXPS spectrum, although the Fe 3d states still contribute largely to the main valence band of the SXPS spectrum. By contrast, the UPS spectrum reveals mainly the transition-metal 3d states.

Since the probing depth for the 900 eV photoexcitation (~ 1 – 2 nm) is three to five times larger than that for the 63 eV excitation (about 0.4 nm, which is comparable with the lattice constant of Fe₂VAl, $a = 0.5761$ nm) (Zangwill, 1988a; Tanuma *et al.*, 1988), the surface effects such as the narrowing and centring (or disappearing of the gap) of the

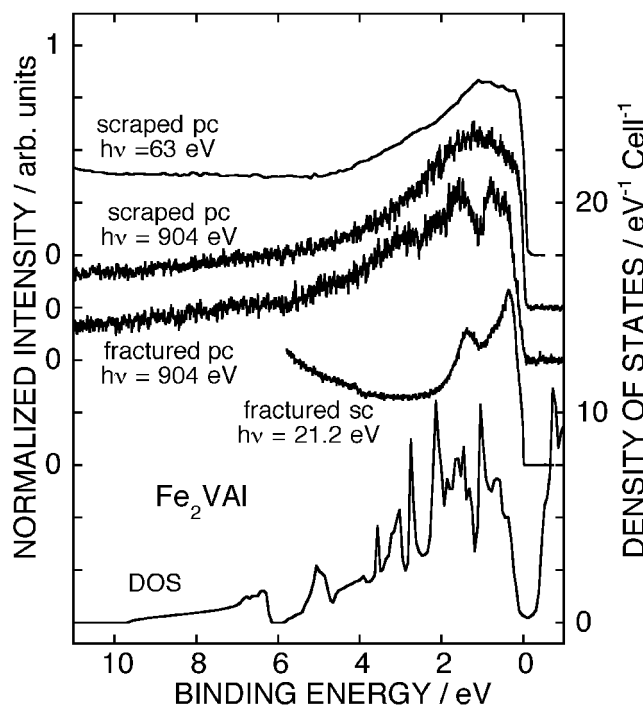


Figure 1 Typical valence band photoelectron spectra for the fractured and scraped surfaces of polycrystalline (pc) and single crystalline (sc) Fe₂VAl specimens. The excitation photon energies $h\nu$ are indicated in the figure. The theoretical density of states (DOS) (Botton *et al.*, 2000) is also shown for comparison.

3d bands in the surface electronic structure (Zangwill, 1988b) are expected for the spectrum recorded with a lower excitation photon energy, but not to affect the SXPS spectrum so much. The surface contribution would be about 10% with a 0.15 nm-wide ($\sim a/4$) surface layer in the present 900 eV case. The valence band width of ~ 2 eV for the 63 eV excitation is smaller than that for the 904 eV excitation (~ 3.5 eV), which may also indicate the surface effect.

The spectral differences between the scraped and fractured surfaces suggest that the electronic structure is highly sensitive to possible strain and defects induced by the scraping of Fe₂VAl. Such degradation or change in the electronic structure has also been found in the magnetic circular dichroism (MCD) measurement at the Fe L_{2,3} X-ray absorption edge, where a fairly large MCD signal, *i.e.* a magnetic moment of $1\mu_B$ on Fe, was observed for the scraped surface of Fe₂VAl in spite of its non-magnetic nature (Yoshimoto *et al.*, 2001). However, very recent MCD measurements with the fractured surface show a reduction of the Fe moment to $\sim 0.1\mu_B$ (Soda *et al.*, 2001). This suggests that the clean surface preparation by the fracture adequately preserves the bulk properties, because Fe₂VAl is in a marginally magnetic state (Kato *et al.*, 2000) and large magnetic moments of $\sim 2-4\mu_B$ are expected for the Fe atom at the site surrounded by eight Fe atoms in the D0₃-type (Fe_{1-x}V_x)₃Al alloy and the magnetic cluster formed around the anti-site defect in Fe₂VAl (Bansil *et al.*, 1999; Deniszczuk, 2001).

The present HRSXPS results directly confirm the existence of a pseudogap at E_F in the bulk electronic structure, which may cause the semiconductor-like conductivity behaviour at high temperatures. Compared with the theoretical DOS, however, the intensity at E_F relative to that of the 3d band around 0.6 eV is much larger than expected and the SXPS spectrum seems to shift by ~ 0.1 eV towards

the lower binding energy side, as shown in Fig. 3. A recent theoretical investigation using a super-cell approach (Deniszczuk, 2001) has predicted that the presence of the magnetic anti-site defect changes the electronic structure near E_F drastically. For the magnetic D0₃-type (Fe_{1-x}V_x)₃Al alloy, the anti-site defect slightly diminishes the width of the pseudogap and leads to the appearance of the peak of the majority spin 3d states at E_F in the mid-gap. For the non-magnetic D0₃-type (Fe_{1-x}V_x)₃Al alloy, the 3d peak at E_F grows and shifts to the higher binding energy side, and a gap of width $\sim 0.2-0.3$ eV opens above E_F . It is suggested that this peak at E_F may cause the unusual electronic, magnetic and transport properties at low temperatures, which are analogous to the 4f heavy fermion system. Thus, the observed shift and relatively large intensity at E_F may indicate a change in the electronic structure corresponding to the non-magnetic state with the anti-site defect, although the expected peak is hardly resolved near E_F in the present photoelectron spectra. As for these mid-gap 3d-derived states, further photoelectron study is now in progress on the slightly non-stoichiometric specimens and will be reported elsewhere.

The present UPS spectrum for the single crystalline specimen is apparently different from the SXPS spectrum for the polycrystalline specimen, although its bulk sensitivity is expected to be comparable with the SXPS spectrum (Zangwill, 1988a). This is partly due to the dominance of the 3d states in the photoionization at $h\nu = 21.2$ eV and probably because of the preference and limitation of the probing k -space for the fractured surface of the single crystal. The slight difference in the composition may also affect the spectral shape. Further experimental study is necessary for this issue at present.

4. Summary

We have investigated the valence band photoelectron spectra of the Heusler-type Fe₂VAl alloy and confirmed the theoretically predicted

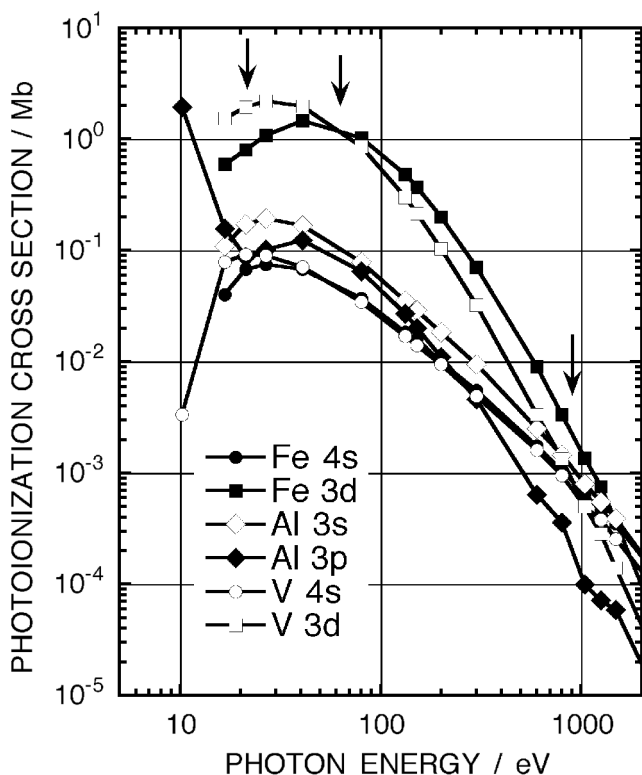


Figure 2 Photon energy dependence of photoionization cross section (Yeh & Lindau, 1985) per electron in the subshells of the constituent elements relevant to the valence band of Fe₂VAl. Arrows indicate the excitation photon energies used for the photoelectron measurement.

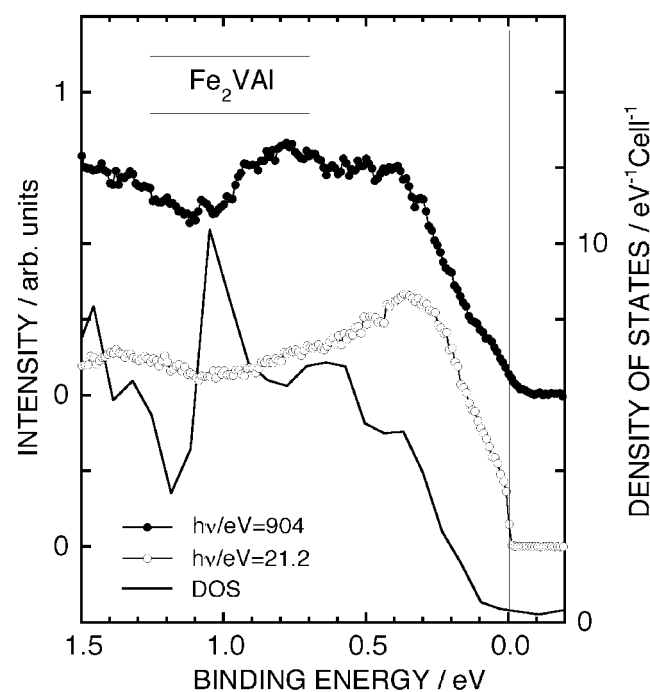


Figure 3 Detailed valence band photoelectron spectra near the Fermi level for the fractured surfaces of Fe₂VAl. The theoretical density of states (DOS) (Botton *et al.*, 2000) is also shown for comparison.

DOS, in particular, the existence of a pseudogap at E_F in its bulk electronic structure, which may cause the semiconductor-like conductivity behaviour at high temperatures. The present study indicates that the electronic structure of Fe₂VAI is highly sensitive to the local structural modification. This suggests that we have to take care to prepare the clean surface by scraping, which has been considered as a simple and convenient preparation method for photoelectron spectroscopy, and shows how useful HRSXPS with a fractured surface is for obtaining the bulk electronic structure.

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