Revealing noncollinear magnetic ordering at the atomic scale via XMCD

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Mass-selected V and Fe monomers, as well as the heterodimer FeV, were deposited on a Cu(001) surface. Their electronic and magnetic properties were investigated via X-ray absorption (XAS) and X-ray magnetic circular dichroism (XMCD) spectroscopy. Anisotropies in the magnetic moments of the deposited species could be examined by means of angle resolving XMCD, i.e. changing the X-ray angle of incidence. A weak adatom-substrate-coupling was found for both elements and, using group theoretical arguments, the ground state symmetries of the adatoms were determined. For the dimer, a switching from antiparallel to parallel orientation of the respective magnetic moments was observed. We show that this is due to the existence of a noncollinear spin-flop phase in the deposited dimers, which could be observed for the first time in such a small system. Making use of the two magnetic sublattices model, we were able to find the relative orientations for the dimer magnetic moments for different incidence angles.

Small magnetic adsorbate systems have been a focus of interest in recent years, as they are promising candidates for high-density data storage devices. Beyond possible applications, the investigation of electronic and magnetic properties of adsorbates provides a way to study coupling phenomena on a fundamental level. It has been shown that the geometric constraints, imposed by a substrate, as well as the hybridization of the substrate with the adsorbate electronic states are often responsible for the appearance of large magnetic moments and anisotropies in magnetic adatoms. Especially in 3d transition metals, a large number of interactions are present at comparable energy scales which leads to a complex behaviour and thus hinders theoretical predictions. It is this complex interplay that is also at the basis of noncollinear magnetic systems.

A prominent example of such complex behaviour are Fe1−xVx bulk alloys, which are found to exist in a complex tetragonal structure called the σ-phase in a V content range from x≈30 at% to 60 at%. It has been shown to behave as a re-entrant magnetic system which, upon lowering of the temperature, undergoes a transition from a paramagnetic to a ferromagnetic state and finally becomes a spin glass. This calls for a closer look into the fundamental coupling between the two constituents. As a prototype model system, we prepared adsorbate systems with small amounts of the respective adatoms and the Fe1V1 dimer on a Cu(001) surface. The choice of Cu(001) is motivated by its sp-like density of states at the Fermi edge and the low-lying d-bands (see e.g.), which provide the possibility for a weak substrate-adsorbate hybridization. Results found for Fe adatoms on Cu(111), where multiplet features have been observed, reinforce this.

The element specificity of X-ray transitions makes XAS a well-suited technique to investigate the electronic structure of compound systems like the present one. Additionally, using circular polarized light makes the absorption signal sensitive to the magnetic moment of the probed element by X-ray magnetic circular dichroism (XMCD). We have chosen to investigate the L2,3 edges, i.e. the 2pj → 3d absorption (with j = 1/2, 3/2) of V and Fe since their electronic and magnetic properties are mainly determined by their 3d levels.

Results and discussion

Fe and V adatoms. First, we will discuss the electronic properties of the Fe and V adatoms on Cu(001). The background corrected absorption spectra across their respective L2,3-edges, as well as the resulting dichroism spectra are shown in Fig. 1c–f. In order to compare the spectral changes, these spectra have been normalized to their respective L3 peak values. For both adatoms, the spectra show features at the lower energy flanks of the respective L3-peak (~515.7 eV and 522.2 eV for V and ~707.4 eV and 721.1 eV for Fe). These multiplet features are the result of the interaction of the 2p core hole and the 3d electrons and are typically found in atomic

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and atomic-like species\textsuperscript{11–13}. Comparison of Fig. 1c–d with XAS of free Fe and V atoms (cf.\textsuperscript{11}) shows very good agreement. The broadening and general energetic shift of the present spectra are due to the reduction of the Slater integrals, which is to be expected for systems showing some degree of hybridization\textsuperscript{14}. The visibility of multiplet features and the resemblance of the spectra to those of free atoms implies a low degree of hybridization of the adatom $d$-states with the Cu(001) surface and ensures that the investigated magnetic properties are intrinsic to the adsorbates.

From the white line spectra, the so called branching ratio (BR) was obtained as the area under the $L_3$ edge divided by the area under the integrated $L_2$, $L_3$ edges. Table 1 summarizes the results for the normal incidence spectra shown in Figs. 1c–d and 4a–b. As the branching ratios obtained in this work are independent of the angle of incidence, we restrict ourselves to the values for $\theta = 0^\circ$. We want to point out, that the determination of the branching ratio for all V species suffers from some uncertainty due to the overlap of the $L_3$ and $L_2$ edges and the somewhat arbitrary separation of the two. However, in the context of this work, it is possible to compare the obtained branching ratios as the edges were separated in the same way consistently.

| Adsorbate | Edges   | BR      |
|-----------|---------|---------|
| Fe\textsubscript{1} | Fe $L_{2,3}$ | 0.83±0.04 |
| V\textsubscript{1}  | V $L_{2,3}$  | 0.66±0.03 |
| Fe\textsubscript{1} V\textsubscript{1} | Fe $L_{2,3}$ | 0.79±0.03 |
| V $L_{2,3}$       |         | 0.58±0.03 |

Table 1. Branching ratios of the adsorbates for $\theta = 0^\circ$ calculated from the white line spectra. Values for other incidence angles are omitted, as the branching ratio is found to be isotropic. For the alloy dimer, the branching ratio is shown for both elements separately.
Considering only spin–orbit splitting in the initial 2p-states of Fe and V, one would expect the absorption intensity from $j = 3/2$ to make up 2/3 of the overall $2p \rightarrow 3d$ absorption intensity. This reflects the statistical degeneracy of the 2p$^j$-levels. However, the presence of spin–orbit coupling in the initial 3d-states as well as electrostatic interactions of the 2p core-hole and the 3d final states tend to change the measured intensity ratio$^{15-17}$. The adsorbed monomers’ branching ratios are, within the error bounds, identical to the ones obtained for free neutral atoms$^{11}$ and cations$^{12}$. They differ substantially from the branching ratios found for the respective bulk materials (BR(Fe)=0.70 and BR(V)=0.50)$^{18}$. It has previously been established that increased screening of the 2p core, e.g. through hybridization with neighbouring atoms, lowers the branching ratio$^{19}$. This is further evidence for a weak hybridization of the adatom and the substrate.

In the following, the magnetic properties of the V and Fe adatoms are discussed by means of the XMCD signals shown in Fig. 1(e–f). Using the well-established sum rules$^{20,21}$, one can extract from the XMCD spectra the orbital magnetic moment $m_L$, and the effective spin magnetic moment $m_{\text{eff}}$, from the sum rules to compare measurements at different incidence angles, as they were all taken at the same magnetic saturation, we can nevertheless refer to the values of the orbital and spin magnetic moments gained from the sum rule results per investigated atoms. Then we only comment on the Fe spin moments. Although it is unlikely that the sample is a single-crystalline material, e.g. through hybridization with neighbouring atoms, lowers the branching ratio$^{19}$. This is further evidence for a weak hybridization of the adatom and the substrate.

Based on the measured in-plane anisotropy of both adatoms, we can gain further insight into the electronic ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling$^{24}$, they follow Russell-Saunders-coupling where the ground state symmetry of the adsorbed monomers by using group theory. As both Fe and V are light transition metals with weak spin-orbit coupling

Figure 2. Orbital magnetic moments (a), effective spin magnetic moments (b) and ratio thereof (c) obtained via the sum rules$^{20,21}$ for the investigated adsorbate systems as a function of photon incidence angle $\theta$. As the V $L_{2,3}$-edges are not separated well enough, only the orbital moments are calculated for those edges. The inset in (b) serves as a reminder of $\theta$ used in this work.

Equations:

$\frac{m_{\text{eff}}}{m_L}$

$m_{\text{eff}} = m_3 + m_7$

$\frac{m_{\text{eff}}}{m_L}$
The $4\text{F}$ term of $d^3$ will split into $^4\text{A}_2 (f_z^3)$, $^4\text{B}_1 (f_{zxy})$, $^4\text{B}_2 (f_{x^2-y^2})$ and two E representations $^4\text{E}' (f_{x^2-y^2})$ and $^4\text{E}'' (f_{3x^2-3y^2})$. This splitting is schematically shown in Fig. 3.

For $3d$ metals, the crystal field splitting is considerably larger than the spin-orbit splitting. Thus, the terms arising from the symmetry lowering will not be mixed or rearranged by spin-orbit coupling and we can identify the $^4\text{E}'$ and $^3\text{E}$ terms as the respective ground states for the Fe and V adatom.

**Fe$_1$V$_1$/Cu(001).** After having discussed the isolated Fe and V adatoms, we will bring both constituents together and study the Fe$_1$V$_1$ dimer. The white line spectra of both elements are shown in Fig. 4a–b for four different values of $\theta$, namely $0^\circ$, $15^\circ$, $30^\circ$ and $70^\circ$. This corresponds to an increased probing of in-plane molecular orbitals. Comparison of the normal incidence spectra with those of the adsorbed monomers shows a clear smearing of the multiplet features. We attribute this to an increased hybridization and subsequent delocalization of the respective $d$-states in the dimer. This is consolidated by looking at Table 1, where a decrease in the branching ratio is observed for both species upon alloying. Due to the delocalization of the $d$-states, their overlap with the $2p$ core hole diminishes, which reduces both the branching ratio and the strength of the multiplets.

Furthermore, the peak positions of the white line spectra shift to lower energies for both elements. For Fe, the $L_3$ peak shifts from 709.0 eV to 708.4 eV, whereas the V $L_3$ changes from 518.0 eV to 517.8 eV upon alloying. This shift is significant, given the energy resolution of $\approx30$ meV of the P04 beamline at these photon energies. Hirsch et al. have attributed such a lowering of the excitation energy to an increased dynamic screening of the $2p$.
core hole by the 3d electrons in the final state\textsuperscript{12}. The more efficient screening is a result of the stronger delocalization and subsequent increased mobility of the 3d electrons. This reduces the energy of the final state, leading to a lowering of the absorption energy. In addition to the overall shift, there is a noticeable energetic shift for Fe when going from $\theta = 0^\circ$ to $\theta = 15^\circ$. We attribute this to a strong contribution of an energetically lower orbital at normal incidence, leading to a shifting center of mass of the whole peak\textsuperscript{27,28}.

Focusing now on the XMCD spectra of both elements shown in Fig. 4c–d, it can be seen that the normal incidence XMCD spectrum of V shows a positive onset at the $L_3$ peak. In combination with the negative sign of the Fe $L_3$ XMCD in the same measurement geometry, this implies an antiferromagnetic coupling between the two constituents’ magnetic moments. This is in accordance with results for Fe/V/Fe trilayer systems\textsuperscript{29} and Fe$_{0.25}$V$_{0.75}$ alloys\textsuperscript{30}, as well as electronic structure calculations of the free FeV dimer, where magnetic moments of $-2.8 \, \mu_B$ and 1.8 $\mu_B$ were found for V and Fe respectively\textsuperscript{31}. We want to note that the shape of the V XMCD is considerably different from the results of Wende et al.\textsuperscript{29} and Scherz et al.\textsuperscript{30}. We explain this discrepancy by noting that the investigated system resembles an atomic species more than a bulk species and that subsequently the XMCD shows notably different features compared to the bulk\textsuperscript{32,33}.

For $\theta = 15^\circ$, the V XMCD signal decreases strongly in magnitude and for incidence angles larger than $15^\circ$, there is a visible sign flip in the V XMCD (cf. shaded areas in Fig. 4c). This indicates a change from antiparallel to parallel orientation of the V magnetic moment relative to the magnetic field. The absence of such an inversion in the Fe XMCD shows that the coupling of the V and Fe magnetic moments is more complex than a collinear (antiferromagnetic or ferromagnetic) configuration. From Fig. 2a it can be seen that the orbital moments of Fe and V in the dimer have the same sign for all incidence angles and we can thus identify the spin-spin interaction of Fe and V as giving rise to the observed noncollinear alignment. $\theta = 30^\circ$ also marks the appearance of a splitting of the $L_3$ peak in the Fe XMCD into two structures, which are well separated for $\theta = 30^\circ$ and can still be distinguished for $\theta = 70^\circ$. Similar to the energy shift of the XAS at $\theta = 0^\circ$ a possible explanation for this is the increased contribution of dimer orbitals of differing magnetic signature when increasing $\theta$. Another possibility is the existence of different adsorption sites of the Fe atoms of the dimer, which in turn couple differently to the V atoms.

To explain the noncollinear configuration, we make use of the two magnetic sublattices model used, for example, in\textsuperscript{37}. Assuming an uniaxial anisotropy, the free energy of a dimer can be expressed by Eq. (1). Here, the first term is the Zeeman energy, the second term is the exchange energy between Fe and V and the third and fourth terms represent the anisotropy energies of the constituents up to second order.

$$E = -B(m_{Fe} \cos(\alpha_{Fe} - \theta) + m_{V} \cos(\alpha_{V} - \theta)) - J_{Fe-V} m_{Fe} m_{V} \cos(\alpha_{Fe} - \alpha_{V}) + K_{uni}^Fe \sin^2(\alpha_{Fe}) + K_{uni}^V \sin^2(\alpha_{V})$$  

(1)

$\alpha_{Fe,V}$ denote the orientation angles of the magnetic moments $m_{Fe}$ and $m_{V}$ relative to the surface normal (cf. Fig. 5). $J_{Fe-V}$ is the exchange constant between the two materials and $K_{uni}$ are their respective anisotropy constants. A stable configuration is found by numerically minimizing Eq. (1) with respect to $\alpha_{Fe}$ and $\alpha_{V}$. Depending on the interplay between exchange coupling and anisotropy, there exists a so-called spin-flop phase in which the magnetic field, applied along the easy axis of the system, causes the magnetic moments to cant away from the collinear case.

In the absence of reported magnetic moments for the present system, $m_{Fe}$ and $m_{V}$ were assumed to be 2.27 $\mu_B$ and 0.99 $\mu_B$, based on the Fe$_{0.25}$V$_{0.75}$ alloy reported in\textsuperscript{30}. Equation (1) was subsequently minimized for large ranges of $K_{uni}^Fe$, $K_{uni}^V$ and $J_{Fe-V}$. The orientation of the magnetic moments is given by $\cos(\alpha_{Fe} - \theta) > 0$ for $\theta \geq 30^\circ$.

An exemplary set of angles which were calculated to recreate the measurements are shown in Fig. 5(b). In this particular case, $J_{Fe-V} = -0.575 \pm 0.005$ meV/$\mu_B$, $K_{uni}^Fe = 1.80 \pm 0.01$ meV/atom and $K_{uni}^V = -0.97 \pm 0.01$ meV/atom. These values were chosen as they also yield similar magnitudes for the V XMCD in the case of $\theta = 15^\circ$ and $\theta = 30^\circ$. While $K_{uni}^Fe$ is significantly higher than the corresponding value of bcc Fe ($K_s \approx 4 \, \mu eV/atom$\textsuperscript{35}), it is still reasonable considering the reduced symmetry of the Fe atom within the dimer. Also, $K_{uni}^V$ is remarkably similar to the value of 1.8 meV/atom found for Fe monomers on Cu(111)\textsuperscript{36}. Isberg et al. found a combined $K_{uni}$ value of 0.3 meV for Fe/V(100) superlattices\textsuperscript{46}. Although it is difficult to compare our results to this overall case, we want to note that the sum of $K_{uni}^Fe$ and $K_{uni}^V$ (namely 0.78 meV) turns out to be less than a factor of 3 off. Multiplying the best fit value of $J_{Fe-V}$ with the assumed magnetic moments of Fe and V, we arrive at an exchange energy of $-1.035$ meV, which is in reasonably good agreement with the antiferromagnetic exchange energy of $-0.94$ meV Poulopoulos et al. found for Fe$_{x}$V$_{1-x}$ superlattices on MgO(001)\textsuperscript{37}.

Conclusions

To summarize, we have studied the magnetic properties of Fe and V adatoms as well as the Fe$_2$V$_3$ dimer on a Cu(001) surface using X-ray spectroscopic methods. The Fe and V adatoms interact weakly with the Cu(001) surface, leading to the appearance of multiplet features in the $L_{2,3}$-edge NEXAFS spectra. From spectra at two different incidence angles, an in-plane easy axis has been seen for both adatoms. The respective orientations of the individual magnetic moments in the dimer have been determined by taking XMCD spectra at different photon incidence angles, i.e. angular resolved XMCD at the corresponding $L_{2,3}$-edges. These results give evidence for the existence of a spin-flop phase already in the magnetic moments in a Fe$_2$V$_3$ dimer on a Cu(001) surface. Employing a simple magnetic model, we were able to determine a set of constants that reproduce the measured behaviour. The magnitudes of these constants are consistent with the weak substrate-adsorbate interaction we found for the respective adatoms. The fundamental dimer system studied in this work already shows a complex noncollinear magnetic coupling and lends itself to the comparison to theoretical models, since many-body effects are less crucial in such a model system.
Going forward, it would be interesting to compare the present results with XMCD measurements on the free Fe\textsubscript{1}V\textsubscript{1} dimer and to perform similar measurements on a wide range of dimer constituents and surfaces to establish systematic information on magnetic coupling at these scales.

**Methods**

The preparation and deposition of monomers and dimers, as well as the X-ray absorption measurements were performed *in situ* and under UHV conditions at the P04 beamline at PETRA III in Hamburg. The low base pressure (≤5×10\textsuperscript{-10} mbar) during preparation and measurement is crucial in assuring that no oxidation of the adsorbates occurs, which would critically alter their electronic structure and magnetic properties. For the same reasons, and to ensure a reproducible substrate, the Cu surface was sputter cleaned and annealed extensively prior to each preparation.

Following, adatoms and clusters were produced by sputtering a FeV target (50/50 at% with purity >99.9 \%) with 30 keV Xe\textsuperscript{+} ions. The cationic sputter fragments were extracted from the sputter region via a potential of 500 V. Mass selection of the fragments due to their mass-to-charge ratio was achieved in a dipole magnetic field perpendicular to the fragments trajectory. The resulting mass spectrum is shown in Fig. 1a. The mass-selected fragments are landed with a kinetic energy of ∼1 eV/atom and a soft landing scheme\textsuperscript{39,40} is employed to avoid fragmentation or implantation of the adsorbates into the substrate. Kr buffer layers were adsorbed onto the substrate at T≈25 K before cluster deposition and desorbed afterward by flash heating to T≈120 K. Figure 1b shows a schematic of the deposition process. The low substrate temperature of ∼25 K in combination with the low coverage of adsorbates on the surface (<0.03 ML), serve to prevent adsorbate diffusion and agglomeration.

The V L\textsubscript{2,3} and Fe L\textsubscript{2,3}-edge spectra of the deposited species were recorded by scanning the photon energy in the ranges of 500–528 eV and 700–730 eV, respectively. For the present case, the energy resolution of the beamline...
was ~30 meV\(^{26}\). The sample drain current, representing the total electron yield (TEY), was used as a measure of the X-ray absorption. To minimize the influence of possible fluctuations of the photon flux on the absorption, measurements were normalized to the TEY signal of an Au grid placed half a meter before the sample.

The XMCD signal was obtained as the difference of absorption spectra for parallel (\(\mu_+\)) and antiparallel (\(\mu_-\)) alignment of the photon wavevector \(\mathbf{k}\) and the magnetic field \(\mathbf{B}\). In contrast to our earlier work on mass-selected adsorbate,\(^{41–44}\) alignment of the magnetic moments was achieved via a superconducting split pair solenoid magnet with maximum magnetic field of \(\pm 7\) T, purchased from Cryogenic Limited\(^{45}\). The polarization of the photon beam was kept fixed and collinear to the magnetic field, which was switched between the two extrema. Angular dependence of the adsorbate magnetic moments was investigated by rotating the sample, while keeping the respective directions of the photon wavevector \(\mathbf{k}\) and the magnetic field \(\mathbf{B}\) fixed, and hence changing the photon angle of incidence relative to the surface normal (\(\theta\) in Fig. 1b).

Given the dilute nature of the adsorbates, the absorption spectrum is dominated by the Cu substrate. As the investigated energy range lies far away from an X-ray absorption edge of the substrate, its contribution is treated as a linear background and subtracted from the spectra. Furthermore, a double step function was subtracted from all the spectra accounting for the absorption signal from Fe and V electrons being excited into sp-like states.

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Author contributions
F.K., I.B., T.B. and M.M. conducted the experiments. F.K. and F.P. analysed the results. All authors reviewed the manuscript.

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