Spectral Momentum Densities of Vanadium and Vanadium Oxide as measured by High Energy (e, 2e) Spectroscopy

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Abstract

The spectral momentum density of vanadium and V_2O_3 is measured by electron momentum spectroscopy. Results are compared with band structure calculations based on density functional theory. Qualitatively the agreement between theory and experiment is good. The calculated total band width of vanadium metal seems somewhat smaller ($\simeq 0.5 \text{ eV}$) than the observed one. The splitting between the outer and inner valence band in V_2O_3 is 2 eV larger in the experiment than in the density functional theory calculation. The observed momentum distributions agree reasonable well with the calculated distribution. The momentum density near the Fermi level in V metal resembles that of atomic V3d orbitals. However momentum profiles of the V3d orbitals in V_2O_3 are much sharper peaked than the atomic 3d orbital in both the theory and experiment. Correlation effects are identified and theoretical problems in describing EMS data from narrow band systems are identified.

 $Key\ words:$ spectral function, electron momentum spectroscopy, band structure, Vanadium, vanadium oxidePACS:79.20.Kz

1 Introduction

Electron momentum spectroscopy (EMS) has shown in recent years that it can measure spectral momentum densities of matter directly[1]. It has a com-

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pletely different foundation compared to angular resolved photo-emission, the standard technique for the determination of band structure. It is a collision experiment and the measured intensity is directly proportional to spectral function of the target. Within a one-particle picture the measured intensity is simply proportional to the probability that a target electron has a certain binding energy, momentum combination.

In the last few years the technique has been tested for several 'simple' cases, that are considered to be well-understood materials. For example single crystals of graphite [2], silicon[3] and copper [4] were studied. In general it became clear that, in spite of multiple scattering, quantitative information can be obtained by EMS, and even for the simple cases reasonable agreement between measurement and theory can only be obtained, if many-body effects are incorporated in the theory.

Now the validity of the technique is well established we want to start focussing on more complicated cases, where band structure calculations fail to predict even the most basic properties of materials. One such example is V_2O_3 a material that has a phase transition from a metallic phase to an insulating phase at low temperatures. This paper describes the first step of this project, a comparison of the EMS spectra of vanadium metal with those of V_2O_3 .

In spite of the somewhat basic sample preparation procedures (polycrystalline thin films supported on a thin carbon film) the technique reveals interesting insights in the electronic structure of these materials. There has been very little theory developed for EMS of narrow band systems. As we show here that these measurements are becoming possible we want to stress the need for such a theory. Several possible experiments that might form a new test for theories are discussed.

2 Experimental Technique

In the high-energy high-resolution EMS spectrometer, which is fully described elsewhere [5], a well collimated beam of 50 keV electrons is incident on a thin self-supporting sample. The incident and struck electrons emerge with nearly equal energies (25 keV) and polar angles (~ 45°) relative to the incident (z) direction. The use of such high energies for the incident and emitted electrons reduces greatly the multiple scattering effects, which plagued earlier measurements [6,7]. The energies and azimuthal angles of the emitted electrons, detected in coincidence, are measured with electrostatic analyzers fitted with two-dimensional position-sensitive detectors [5]. In high-energy EMS the incoming and outgoing electrons can be accurately treated as plane waves. Knowing their energies E_i and momenta \mathbf{k}_i one can infer the binding energy ω and momentum \boldsymbol{q} of the struck electron before the collision through the conservation laws

$$\omega = E_0 - E_1 - E_2, \qquad q = k_1 + k_2 - k_0, \tag{1}$$

where the subscripts i = 0, 1, 2 refer to the incident and emitted (scattered and ejected) electrons, respectively.

If the mean scattering plane (horizontal) is defined as the x - z plane, then the momentum component q_y is determined by the relative azimuthal angles ϕ_1 , ϕ_2 of the two detected electrons. The momentum components in the xand z-directions are determined by the choice of polar angles θ_1 , θ_2 . In the present case the polar angles were both fixed at 44.3° so that $q_x = q_z = 0$. Different choices of θ_1 and θ_2 about 44.3° give other values for q_x and q_z , in which case the measurements are along lines in momentum space that do not go through q = 0 (a Γ point) [5].

In EMS the measurement involves real momenta and it does not depend on the crystal lattice, it applies as well for (gas-phase) atoms and molecules, single crystals, amorphous materials as it does for the present polycrystalline samples. For the polycrystalline samples we can measure the spherically-averaged spectral function. The spherically-averaged spectra will generally be broader and show less structure than those obtained for a single crystal. However the spectra at zero momentum is not affected by the averaging procedure. The energy and momentum resolution are 1.0 eV and 0.1 a.u. respectively.

EMS is a transmission spectroscopy that requires extremely thin free-standing films. Vanadium metal films were evaporated on a thin (30 Å thick) free standing amorphous carbon film. The thickness of the vanadium layer was approximately 100 Å, as judged from the crystal thickness monitor. Some of the (e,2e) events will occur in the carbon layer. This will cause a signature of the carbon spectral function in the data. However in that case two electrons have to traverse the vanadium layer, with a relatively high probability of elastic and inelastic scattering. Thus the contribution of the carbon layer is less than that expected just from the ratio of the thicknesses. The signature of the carbon layer can by subtracted, in first approximation, using the measured spectral function of a carbon film.

 V_2O_3 films were obtained by evaporating in a oxygen atmosphere (10⁻⁷ torr). This is known to produce samples with a stoichiometry of V_2O_3 (see e.g. [8]). No clear influence of annealing on the measured data was observed, indicating that the measured electronic structure is not very sensitive to the degree of long-range order.



Fig. 1. Measured (left half) and calculated (right half) spectral momentum densities of a vanadium film and a V_2O_3 film

3 Theory

to be expanded/rewritten by Anatoli FP-LMTO calculations were done for both V metal (BCC structure) and V_2O_3 (Corrundum structure) as described in [9]. From the obtained band structure we calculate the energy resolved, spherically-average momentum density. The spherically-averaging is required due to the fact that we have polycrystalline samples. This distribution is convoluted with an energy resolution of 1 eV, and this can be compared with the experiment. For the V metal case we also did calculations incorporating a semi-empirical life-time broadening, with the Lorentzian broadening dependent on the binding energy of the electron. The band structur obtained for V_2O_3 was in good agreement with the calculations published by [10].

4 Experimental Results

In Fig. 1 we show the measured spectral function of the vanadium metal film and the V_2O_3 film. A faint contribution of the carbon spectrum was subtracted. The data are compared with the results of the full-potential Linear Muffin Tin Orbital (FP-LMTO) calculation [9]. The calculation was convoluted with an experimental energy resolution of 1 eV. The same main features are evident in the experiment and theory, but the experimental distribution is broader (due to life time broadening and finite momentum resolution) and



Fig. 2. A comparison of the spectra for vanadium metal and V_2O_3 for momentum intervals as indicated. The insert shows spectra near zero momentum for the 100 Å thick vanadium sample and a thinner vanadium sample, both supported by a 30 Å thick carbon film.

the contrast is less (due to multiple scattering). The vanadium metal results show a free-electron parabola, evolving in a broader, less intense distribution near the Fermi level. The free-electron part is due to the s-electrons whereas the broader distribution near the Fermi level has mainly a 3d character.

The sample obtained by evaporation in a oxygen ambient has a completely different distribution. Here the two main components are mainly derived from the O 2p levels(near 8 eV) and the O 2s levels (near 22 eV). There is a weak signal, hardly visible in these grey-scale plots, just below the Fermi level, originating from V 3d electrons. Within the O 2p related intensity, and to a minor extend in the 2s related intensity, there is clear change in binding energy with momentum (dispersion). The 2s level has maximum binding energy and intensity at zero momentum, whereas the 2p level intensity approaches zero, and a minimum in binding energy. This behavior is typical for the O2p and O2s derived orbitals in oxides [11]. In the grey-scale plot we showed only the valence band region. However the experimental data contained also the outer core levels of Vanadium (3p and 3s). These core levels are more diffuse in momentum space, and hence a weaker signal is obtained. Reasonable statistics can be obtained by integrating the data over an 0.5 or 1.0 a.u. wide momentum range. This is done in Fig. 2.

It is in these measurements often a bit problematic to pinpoint the exact Fermi level position, as the shape of the spectra is determined by both energy and momentum resolution [12]. In the V metal spectra the V 3p level stands out as a relative sharp feature and this is the easiest way to fix the energy scale. Using a binding energy of 37.8 eV for this level [13] we obtain the present energy scale. In contrast to XPS we resolve the momentum of the core level. Thus, in theory, dispersion of the V3p level could be measured. In contrast to the O2s level there is no sign of dispersion in the V2p binding energy. This sets an upper limit to the dispersion in the V 3p level of 0.25 eV.

The insert shows the spectra near zero momentum of the 100 Å thick film together with that obtained from a much thinner film. For this film we can distinguish clearly three peaks, the peak at large binding energy resembles the spectra of carbon near zero momentum, both in position and shape [14]. The low binding energy peak lines up with the Vanadium peak of the thick sample. The middle peak we assign to a carbon-vanadium peak at the interface. Its sharpness indicates that a well-defined phase has formed at the interface. Its contributions of both the carbon peak and the interface compound peak can be distinguished in the thick Vanadium sample as well, but are much weaker. Using a measured spectral momentum density of a thin carbon foil we can eliminate the carbon peak by subtracting the appropriately scaled carbon intensity distribution. This was done for the results displayed in Fig. 1

For the oxide spectra the V 3p and 3s core levels are much broader, a fact that is well known from XPS data [13]. It is therefore not a convenient way of fixing the energy scale. We put the Fermi level near the leading edge of the V 3d feature. The broad V3p feature of the oxide is then several volts higher binding energy of the metal, an agreement with the XPS data.

This large width of the core levels in V_2O_3 is often attributed to interaction between the core hole and the V 3d electrons in their narrow band. The 3d electron is localized on the V atom with the 3p core hole. The energy of the final state depends than on the total angular and spin momentum (multiplet structure) [13].

Within the limits of statistical accuracy we see no dependence of the V 3p line shape on momentum. Also the momentum distribution follows a typical p-type behavior (a sharp minimum at zero momentum). The momentum measured in an EMS experiment is the recoil momentum, ie the total change in momentum of the target. If as a consequence of the ionization a valence electron is localized one would expect the total momentum transferred to the target to be different from that of the ejected core electron by itself. If the excess width is due to an unresolved multiplet states then final states with different angular momenta could have different recoil momentum. No theoretical models describing these



Fig. 3. Spectra for selected momentum intervals (left panel) and momentum densities for selected binding Energy intervals (right panel) for a V metal film. The solid line is obtained from the LMTO theory integrated over the same range as the experimental spectra. The dashed line in the right panel is integrated from 6.5 to 7.5 eV, corresponding to the peak position at zero momentum in the calculations

cases have been developed so far.

The current measurements were done with the maximum sensitivity in the valence band region. By increasing the energy of the impinging electrons by the binding energy of the 3p electrons we can increase the sensitivity of the spectrometer in this region [15]. Existence of a theoretical model would certainly be a motivation for doing more accurate measurements of the V 3p core level. EMS could provide here a different test of theory of the electronic structure, than is possible in XPS.

In Fig. 3 we show more spectra of V metal at selected momentum intervals, as well as momentum distributions at several binding energy intervals. These experimental results are compared with an LMTO calculation convoluted with 1 eV energy resolution. This theory underestimates the width of the observed spectra, especially at larger binding energies. This is mainly due to life-time broadening. In spite of this it appears that the theory underestimates the total band width by 0.5 eV. This is in contrast to copper where the observed total valence band width as measured by EMS or photoemission exceeds the width predicted by the FP-LMTO theory by about 0.6 eV [4]. Unfortunately the few angular-resolved photoemission studies published for vanadium metal do not alow for the determination of the full band width, as the spectra are dominated by emission from the d electrons [16].



Fig. 4. Spectra of V_2O_3 for the valence band region for momentum intervals as indicated.

Also shown in Fig. 3 is the results of the FP-LMTO theory convoluted with a semi-empirical life time broadening. This improved the overall agreement between theory and experiment considerably. The main discrepancy is now a smooth background due to inelastic multiple scattering and intrinsic satellites. No attempt has been made yet to disentangle both contribution, a problem that is complicated due to the presence of an interface component in the sample. Generally the intensity near the Fermi level (mainly d electrons) and at larger binding energy are described reasonably well by the theory.

Now let us have a closer look at the valence band of V_2O_3 . The spectra for selected momentum intervals are plotted in fig 4. The observed structures are considerable wider than our energy resolution. Therefore we convoluted the calculated spectra with an energy resolution of 3 eV and plotted these calculations in the same graph. There are two obvious discrepancies between the calculated and measured distributions.

In the first place the separation between the O 2s and O 2p parts of the valence band is larger in the experiment than predicted by the FP-LMTO method by about 2 eV. This discrepancy is not unique for V_2O_3 , but is observed for all oxides studied by EMS[17–20]. It could be a problem related to density functional theory (DFT). Band gaps in semiconductors are always underestimated in DFT calculations. The underestimation of the gap between the inner and outer valence band of the oxides may have the same roots. A GW calculation of these oxides would be desirable. Indeed for the ionic compound LiF Shirley et al.found that quasiparticle calculations within the GW scheme gave a 1.7 eV larger separation of the F 2s and 2p bands than a band structure calculation within the DFT scheme [21]. The observed discrepancy for V_2O_3 is thus in line with the calculated self-energy effects in LiF.

A second discrepancy that is also observed for all other oxides studied by EMS is that the ratio between the observed intensity in the O2p derived band relative to that in the O2s derived band is off by at least a factor of two. This is obvious in Fig. 4. The maximum intensity of the s level is at zero momentum. In the experiment the maximum 2p intensity is near 0.8 a.u. The 2p intensity near 0.8 a.u. is nearly the same as the 2s intensity at 0 a.u. However the theory predicts that the maximum 2s intensity exceeds the 2p intensity by about a factor of 3. We can consider the measured peaks to be on a smooth background due to multiple scattering. Visual inspection makes clear that only considering the peak above the background increases the problem, rather than decreases it (there is more background under the maximum of the 2s peak, than at the maximum of the 2p peak. Again all studied oxides display a similar pattern.

From gas-phase measurements we know that for example in the case of argon a considerable amount of intensity associated with the 3s electrons appears in the form of satellites at higher binding energy [22]. Only 5% of the Ar 3p intensity appears in the form of satellites, whereas 45 % of the 3s intensity is appears as a satellite. Considering the oxygen ions as a closed shell system, we could expect similar values here. Unfortunately we can not distinguish between the background due to inelastic multiple scattering (energy loss of the incoming or outgoing keV electrons) and that due to satellites. Moreover for the case of Neon, which resembles the oxygen ions much more closely, the gas-phase measurements show a satellite intensity of the 2p level of 8% and for the 2s level 15% [23]. This would change the intensity ratio only marginally. Hence the observed intensity distribution of the oxides are still puzzling.

To see if the momentum dependence of the intensity of the levels can shed any light on the problem we fitted the peaks as a Gaussian on a linear background. The area of the Gaussians is plotted in Fig. 5. The theory has been normalized to the experiment separately for the 2p level and 2s levels. The measured shape compares well. The 2p level shows, as expected a sharp minimum at zero momentum as this corresponds to a node in the wave function. Such deep minima are only observed after careful alignment of the scattering geometry[24]. The residual intensity is in line with expectations and due to finite momentum resolution and low levels of elastic multiple scattering present even at the high electron energies deployed here. The intensity distribution integrated over the 2s and 2p part resembles the atomic 2s and 2p levels for



Fig. 5. The measured intensity for the O2s, O2p and V 3d part of the spectrum, compared with the calculated density

both the experiment and the FP-LMTO calculation. We also plot in Fig. 5 the intensity distribution of the shoulder near the Fermi level. The shoulder is due to the V 3d derived bands. It is a weak signal on a broad background. However the experiment and theory both show a relatively sharp feature at 1.2 a.u. It is much sharper than the atomic V 3d distribution. The fact that the FP-LMTO predict it correctly means that the electrons are coherent i.e. can be represented by Bloch functions.

Replacing a few % of vanadium by chromium in V₂O-3 causes a change from an metal to an insulator (see e.g. [25,26]). This phase transition is often considered to be a prime example of the transition from a metal to a Mott-Hubbard insulator. The current sharp peak in the momentum distribution near E_f for the metal phase is a consequence of the Bloch nature of these electrons (band structure effects). In the insulating phase, not predicted by band structure calculation, the electrons are considered localized (incoherent), and intuitively one would expect a momentum distribution to be more like that of an isolated atom (much broader). Thus these realistically possible experiments could provide a new window on the Mott-Hubbard phase transition.

In spite of the polycrystalline nature there is a clear dispersion int the outer valence band. The theory predicts that more than one component should be visible at a given momentum. To demonstrate this we plot the outer valence band only in Fig. 6, together with the theory convoluted by only 1 eV energy resolution. Between 1.2 and 1.4 a.u. of momentum there is a shoulder visible in the experiment, just below the Fermi level. The theory has a separate peak



Fig. 6. The outermost valence band region for V_2O_3 , for momentum intervals as indicated.

with similar intensity. It is this shoulder that causes the peaks in the V3d momentum distribution, as plotted in the top panel of fig. 6.

The main intensity of the experiment, due to the O2p part of the valence band follows the shape of the theory nicely, but is generally not as sharp as one would expect based on a one 1 eV energy resolution. Life-time broadening is expected to be minor here, as there are no wave functions at lower binding energy with a large density at the oxygen ions. The presence of more than one phase could be the origin of these problems, as the V-O phase diagram is very rich.

5 Conclusions

We report on preliminary EMS experiments on vanadium and one of its oxides. In spite of the simple sample preparation procedure followed it is obvious that for the V_2O_3 it is a potentially rich source of new information. We plan to grow higher quality samples. Epitaxial films can be grown on Au(111) surfaces [8]. Free standing Au(111) films can be grown straightforwardly on NaCl. By removing the Au film by sputtering we can obtain single crystal V_2O_3 films. A free-standing conducting single crystal target may be of help resolving the long standing problem of reconciling the calculated 2p/2s intensity ratio with the observed one. The other obvious experiment is co-evaporation of small amounts of Co together with Vanadium in an oxygen atmosphere, forming a Mott-Hubbard insulator. The momentum distribution observed under these conditions at small binding energies are expected to be different from those observed for pure V_2O_3 . The broad V 3p peak in V_2O_3 is another challenge. Should it have the same momentum distribution as the atomic 3p peak, or, assuming it is due to interactions with the V 3d electrons, does it have a different momentum dependence, or will its shape depend on energy? Theories describing these phenomena would certainly stimulate further experimental endeavors.

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