



Probing the spectral densities over the full three-dimensional momentum space

M. Vos*, V.A. Sashin, C. Bowles, A.S. Kheifets, E. Weigold

*Atomic and Molecular Physics Laboratories, Research School of Physical Sciences and Engineering,
The Australian National University, Canberra ACT 0200, Australia*

Abstract

Electron momentum spectroscopy is often used to determine the spectral function of materials. It relies on the determination of the scattering angle of electrons with extremely high precision. In practice, it is important to calibrate these angles, and hence the momentum scales. Here we describe a method to do so and show how minor misalignments affect the measured momentum densities of Li_2O . Using the same procedure we further calibrated the momentum scale by measuring the spectral momentum density along a Brillouin zone boundary of a Si single crystal.

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1. Introduction

In an electron momentum spectroscopy (EMS) experiment an incoming electron with keV energy ionizes a target and the scattered and ejected electron are detected in coincidence. By comparing the incoming and outgoing kinetic energies one can calculate the energy ε transferred to the target in the ionizing event. By comparing the incoming and outgoing momenta one can determine the recoil momentum \mathbf{q} (i.e. the momentum transferred to the target in the ionizing event). The frequency that a certain event (ε, \mathbf{q}) occurs is proportional to the magnitude of the spectral function at that (ε, \mathbf{q}) combination. In a one-particle picture, ε corresponds to the binding energy of the orbital ϕ , whereas the observed momentum distribution at that binding energy is proportional to $|\phi(\mathbf{q})|^2$, i.e. proportional to the modulus square of the wave function in momentum space.

EMS of solids has made tremendous developments over the last 30 years. In the pioneering studies of Camilloni et al., only the core electrons were resolved from the valence

band and different momentum distributions for core and valence electrons were seen [1]. Ritter and co-workers showed that the momentum distribution of dispersive structures within the valence band could be resolved [2]. Nowadays we can clearly see the effects of electron–electron correlations in the energy-resolved valence momentum densities [3,4]. In all these studies, multiple scattering formed a significant obstacle. It had to be minimized by the use of high kinetic energies of the electrons involved, combined with extremely thin targets (≈ 10 nm). In our current spectrometer we use energies of 50 keV for the incoming and 25 keV for both outgoing electrons [5,6]. The magnitude of the momenta of these electrons are large [62.07 a.u. (117.3 \AA^{-1}) for the incoming electron (\mathbf{p}_0) and 43.36 a.u. (81.9 \AA^{-1}) for the outgoing electrons ($\mathbf{p}_{1,2}$)]. To determine \mathbf{q} , the recoil momentum (which corresponds for uncorrelated electrons to minus the momentum of the struck electron *before* the collision), one has to determine the vectorial difference of the incoming and outgoing momenta: $\mathbf{q} = \mathbf{p}_0 - \mathbf{p}_1 - \mathbf{p}_2$. Here \mathbf{q} is a relatively small vector (of the order of 1 a.u. for sp valence electrons). Thus, a small vector is determined by the subtraction of much larger vectors. An accurate value of \mathbf{q} can only be obtained if the magnitude *and* direction of $\mathbf{p}_{0,1,2}$

* Corresponding author.

E-mail address: maarten.vos@anu.edu.au (M. Vos).

are precisely known. The magnitudes of $p_{0,1,2}$ are known with extreme precision, as these are determined by their kinetic energies which are measured with a precision of ≈ 0.4 eV. The accuracy of the momentum determination is thus dependent on how well the scattering angles are determined.

In our spectrometer we aim at a total momentum resolution of 0.1 a.u. (i.e. $\Delta q_x^2 + \Delta q_y^2 + \Delta q_z^2 < (0.1)^2$ a.u.²) which means that we have to know the directions of the incoming and outgoing electrons extremely well. For example, a deviation of the incoming beam direction of 0.1° corresponds to a momentum error of 0.1 a.u. Hence extreme care was taken to align the collimator of the incoming beam relative to the slits that determine the outgoing trajectories. Moreover, to ensure that the electrons move along straight lines, it is important to minimize stray magnetic fields. The vacuum chamber was completely surrounded by co-netic, a magnetic shielding material, to reduce the magnetic field in the chamber to less than 5 mG.

In spite of these precautions, it is still important to be able to test if the actual momentum q measured corresponds to the expected value. Significant deviations of the actual from the designed collision kinematics were found for solid state EMS spectrometers in the past [7]. For the present spectrometer, this test can be done using two double deflector sets, one for each analyzer. Moreover, these deflectors can be used to access certain momenta on purpose, allowing probing of the full three-dimensional momentum space. The description of this setup, and the demonstration of its working in practice, is the subject of the rest of this paper.

2. Spectrometer details

The spectrometer has a non-coplanar symmetric configuration (see Fig. 1). This means that the scattering angle of both detected electrons is identical ($\theta = 44.3^\circ$), but the momentum of the ejected electron is not necessarily in the plane defined by the incoming and scattered momentum vectors. For 50 keV incoming and 25 keV outgoing electrons, the recoil momentum is zero if all three trajectories are in the same plane ($\phi_1 = \phi_2$). If these trajectories are not in the same plane then, to a good approximation, the recoil momentum is directed along the spectrometer y-axis and its magnitude is proportional to $\phi_1 - \phi_2$.

Each double deflector can change the effective scattering of angle by $\pm 1^\circ$. This is sketched in Fig. 1(b). Thus if, due to construction imperfections, the geometry without deflector voltages of coplanar events ($\phi_1 = \phi_2$) does not correspond to $q = 0$ we can use the deflectors to effectively change the collision geometry in such a way that $q_x = 0$ and $q_z = 0$. The value $q_y = 0$ is always included, due to the use of analyzers that measure simultaneously a range of ϕ angles.

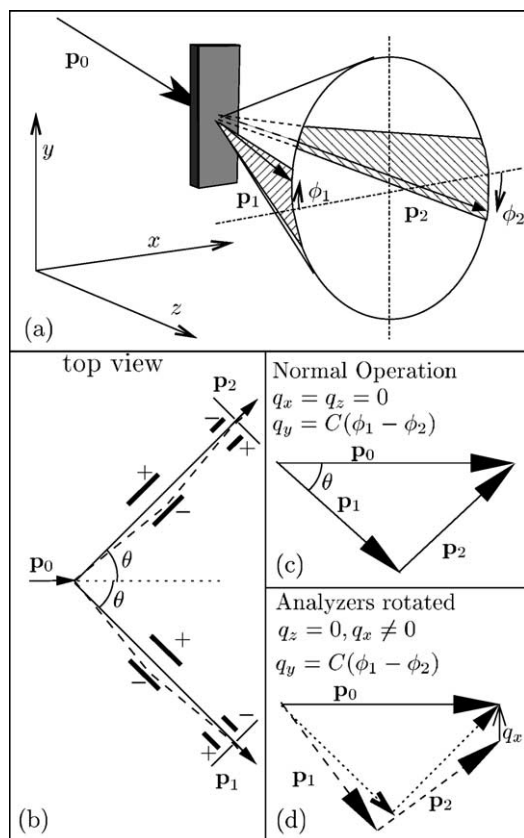


Fig. 1. The EMS spectrometer and the working of its deflectors. In (a) we show the geometry of the experiment. Scattered and ejected electrons with momenta in the hatched area are detected. In (b) we show the top view (looking down along the y-axis) with the scattering angle θ that can be varied by two sets of deflectors (dashed lines are trajectories with deflectors switched on). In (c) we show that the scattering angle θ is chosen in such a way that the recoil momentum is along the y-axis and proportional to $\phi_1 - \phi_2$. By applying voltages to the deflectors one can change the scattering angle and measure also the momentum densities for momentum values with either one or both components of $q_{x,z} \neq 0$ (d).

This offset component can be determined directly as the observed intensity distribution is symmetrical in q_y .

A cut of the electron optics for one of the two detectors is drawn to scale in Fig. 2. The first deflector (D1) is centered 6 cm away from the target. It has a length of 20 mm, and the plates are separated by 3.5 mm. The whole deflector is surrounded by a metal sheet kept at the same potential as the collision region, to avoid any influence of the potential applied to the deflector on the electron trajectories outside the deflector. The opening slits (at the entrance and exit) of this shield are 2.5 mm wide. The second deflector (D2) is centered 12 cm away from the sample, has identical plate separation, but only half the length of D1. Again, this deflector is surrounded by a metal shield at the potential of the collision region. The 0.5 mm wide momentum selecting slit (S) (slightly curved to follow the 44.3° cone, see Fig. 1(a)) is positioned 2.5 cm behind the center of deflector D2. If the same potential, but with opposite polarity is applied to both deflectors then the electron trajectory

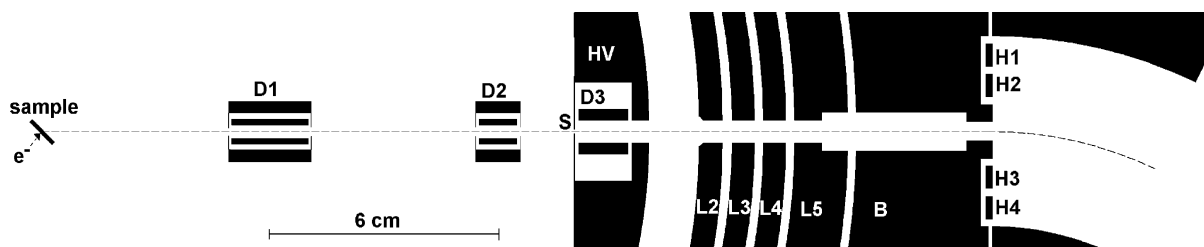


Fig. 2. The electron optics for one of the two analyzers. D1 and D2 are the deflectors for adjusting the collision kinematics, S is the 0.5 mm wide slit that determines which electrons are detected. D3 is an additional deflector, HV is a part of the high voltage sphere, L2–L5 are electrostatic lenses, B is the baseplate of the analyzer, H1–H4 are hoops for correcting the fringe fields inside the analyzer.

transmitted through the slit looks like the dashed trajectory in Fig. 1(b). Thus the transmitted electrons travel through slit (S) along the center (optical axis).

Electron optics simulations were done using the SIMION 6.00 program. Applying ± 100 V to the first deflector and ∓ 100 V to the second deflector results in transmission of 25 keV electron through slit (S) that originated at the sample at an angle of 0.78° with respect to the optical axis. This corresponds to a momentum change of the transmitted electron by 0.59 a.u. relative to those transmitted without deflector voltages.

In order to energy-analyze the electrons with sufficient accuracy it is necessary to decelerate them to the pass energy of the hemispherical analyzers of 400 eV. This deceleration occurs after leaving the high voltage sphere (at +24.5 keV) and the lens system L2–L5 ensures that a focused image is formed at the entrance of the analyzer (with a baseplate (B) at a potential of -100 eV). This large deceleration, especially in the main first step from the HV sphere to L2 (at potentials of 24.5 keV and ≈ 3 keV, respectively) results in some steering action on the beam due to minor mechanical imperfections. This can cause the electrons to travel off-center along the lenses L2–B increasing the aberration of the optics and in extreme cases limiting its transmission. In order to correct for this, we introduced an extra deflector D3, *after* the momentum defining slits. This deflector is used to optimize the energy resolution, in practise by looking at 25 keV incoming electrons scattering elastically from the target. In this way we can measure peaks from elastically scattered electrons from heavy atom targets with a width of 0.4 eV.

3. Results

For EMS studies of gas-phase targets the outermost p levels of a noble gas (e.g. Ar 3p, see e.g. [8]) are usually used to test the momentum resolution of a spectrometer. The wave function of a p orbital changes sign for $q=0$ resulting in a very sharp minimum in the momentum density. The depth of this minimum is a very good indication of the performance of the spectrometer. For solids we can approximate this case by studying ionic compounds, in our case we studied Li_2O . The O^{2-} ion is isoelectronic with neon, and the outermost orbital

of Li_2O will resemble a 2p orbital. Indeed calculations show vanishing momentum density at zero momentum [9]. In the previous published Li_2O data, the minimum of the EMS spectra was rather disappointing (at $q=0$, there was still 38% of the maximum intensity [9]), and hence the deflectors were used to see if this could be attributed to misalignments within the spectrometer. Rather than looking for the minimum directly we measured four spectral momentum densities (SMDs) with deflectors settings corresponding to 0.45 a.u. away from zero momentum along the $\pm p_x$ and $\pm p_z$ directions. For a randomly oriented target, all four spectra should be identical. However if the assumption that spectral momentum densities with $p_x=p_z=0$ would be measured without deflector voltages ($V_1=V_2=0$) was wrong then the four SMDs will not be identical, the one closest to $p_x=p_z=0$ will have lowest intensity in the 2p orbital at $p_y=0$. Judging from the observed differences one can make a new assumption that measurements with deflector voltages $V_1=a$ and $V_2=b$ correspond to the MD with $p_x=p_z=0$. This assumption is tested by measuring four spectra with deflector voltages varied symmetrically around (a, b) . This procedure is repeated a few times until a set of four identical SMDs is obtained, and a measurement for zero momentum can then be done by applying the latest voltages (a, b) to the deflectors.

The deflector voltages required for the most pronounced minimum in the O 2p level turned out to be 12 ± 5 V for one detector and 42 ± 5 V for the other. These (or very similar) values apply to all samples tested. It would correspond to angular misalignments of 0.1 and 0.3° , respectively. As can be seen in Fig. 3 the SMD obtained now had a considerably more pronounced minimum at $p_y=0$ ($\approx 20\%$). This minimum is still less pronounced than that found for Ar of about 7% [8]. However even for the thinnest solid state targets some elastic multiple scattering is present, smearing out the minimum at $p=0$. Hence, the minimum of 20% in the outer valence band of Li_2O is probably as good as one can reasonably expect. It is also clear that the dispersion increases slightly with improved alignment. For completeness, we also show the lower valence band. It is mainly derived from the oxygen 2s electrons. Its measurement is clearly less sensitive to alignment errors. Similar alignment problems may be the origin of the reported deviation of the outer valence intensity in BeO at small momentum

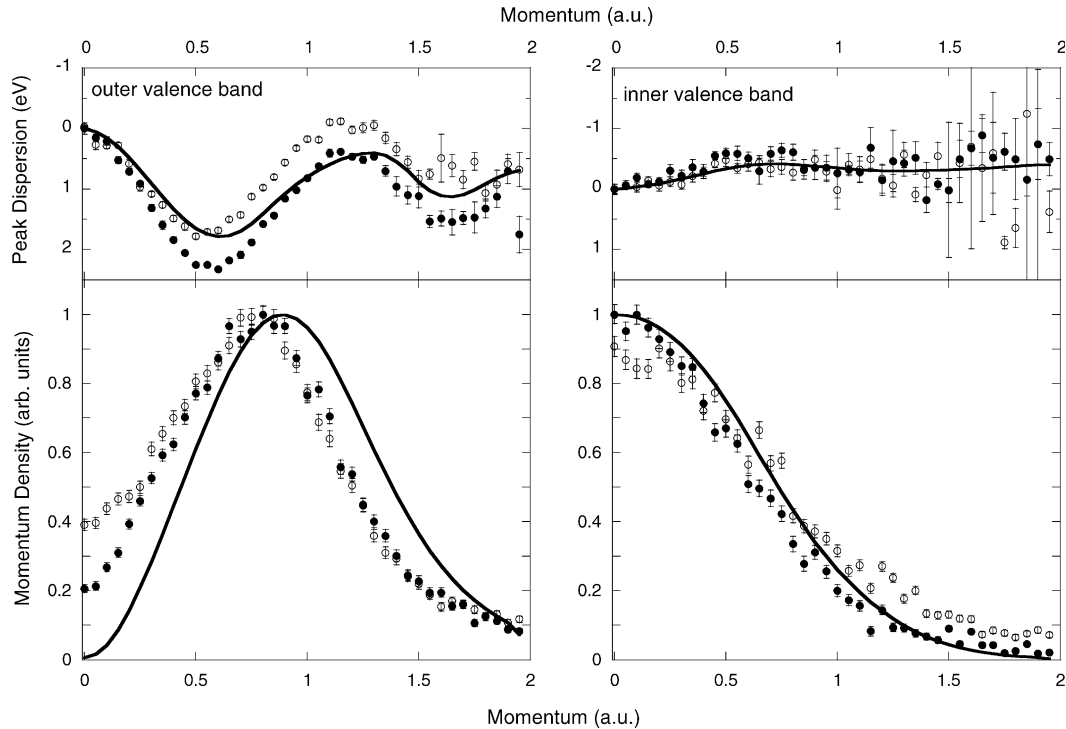


Fig. 3. Dispersion (top) and momentum density (bottom) of the outer (left) and inner (right) valence band of Li_2O . The full line is the theoretical calculation, the open symbols refer to the measurement without the use of deflectors while the filled symbols refer to the measurement with deflectors used to correct the spectrometer alignment. The outer valence band (mainly oxygen 2p derived) is more sensitive to spectrometer alignment than the inner (mainly oxygen 2s derived) valence band. The lower momentum density of the outer valence band at zero momentum is a good indication of the spectrometer alignment.

values as measured by Sashin et al. [9] rather than shortcomings in the theoretical description as suggested by Soul de Bas et al. [10]. Similar remarks apply to the interpretation of the high intensity of the outer valence band of Na_2O at $q=0$ [11].

Having established the conditions for measuring spectral momentum densities with $p_x=p_z=0$ it is interesting to establish with what accuracy we can measure spectral momentum densities with specific p_x, p_y values. Here the test cases are less well established. We choose a silicon crystal with a $\langle 001 \rangle$ surface normal, with the spectrometer y -axis aligned with the $\langle 110 \rangle$ direction of the crystal. For more details about the silicon single crystal EMS measurements see [12].

A cut through the first four Brillouin zones along $p_z=0$ is shown in Fig. 4. If we shift the measurement line by 0.65 a.u. along the $\langle 1\bar{1}0 \rangle$ direction (i.e. the spectrometer x -direction) it coincides with the Brillouin zone boundary. This is accomplished by changing the deflector voltages by 77 V to each set of deflectors (relative to the $p_x=p_z=0$ a.u. measurement), with polarity as shown in Fig. 1(d). The results are shown in Fig. 5.

The $p_x=p_z=0$ measurement shows a single dispersing feature. Around $p_y=0.65$ a.u. ($p_x=p_z=0$) the dispersing feature is split due to the simultaneous crossing of the $(\bar{1}\bar{1}1)$ and $(\bar{1}\bar{1}\bar{1})$ Brillouin zone boundaries. This momentum value correspond to a K point of the band structure. Another K point can be reached at $p_x=0.65, p_y=0, p_z=0$ by changing both

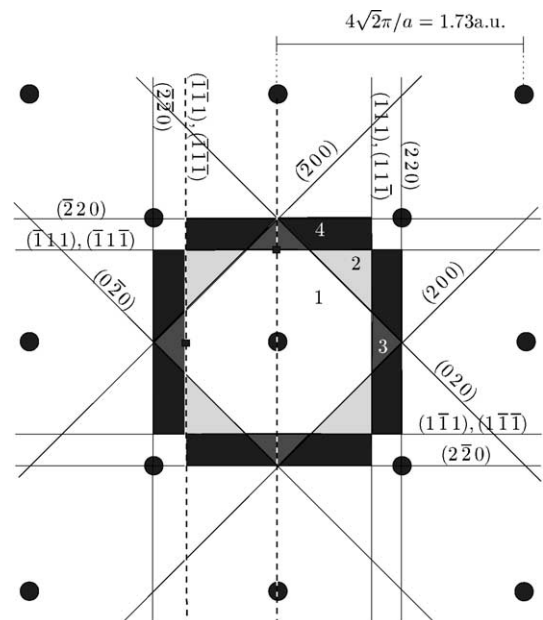


Fig. 4. A cut through the first four Brillouin zones of Si for $q_z=0$. The Brillouin zone boundaries are labeled by the reciprocal lattice vectors the boundary bisects. The right dashed line corresponds to the 'standard' EMS measurement including zero momentum. The left dashed line is for the EMS measurements with the deflectors tuned in such a way that the measurement line in momentum space coincides with a Brillouin zone edge. Note that the momentum values indicated with black squares, at the edge of the first Brillouin zone, are equivalent and should result in identical measurements.

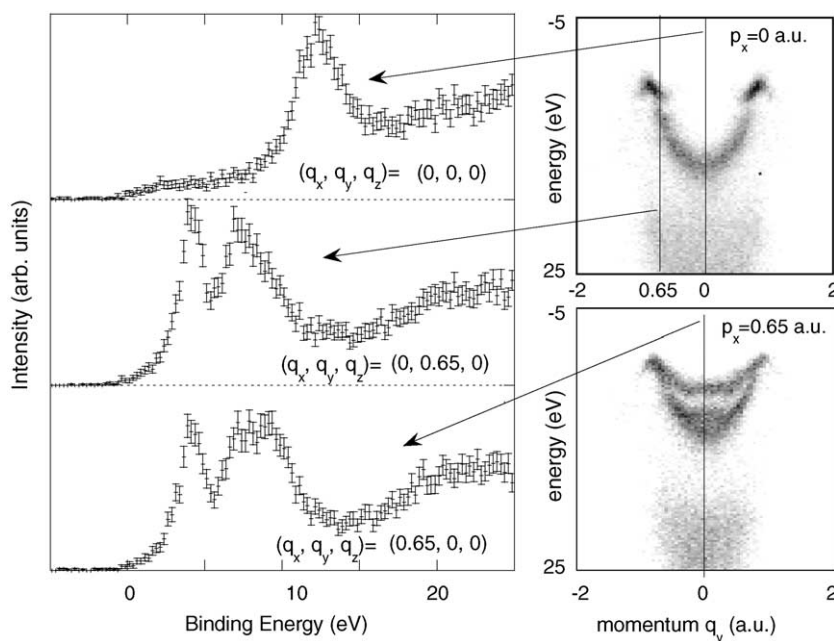


Fig. 5. Comparison of spectra taken at zero momentum (top, left panel) and at two equivalent positions $(0, 0.65, 0)$ (a.u.) (middle) and $(0.65, 0, 0)$ (a.u.) (bottom). The spectra are obtained from two measurements, one with the deflector voltages corresponding to zero momentum displayed as a grey-scale intensity plot in the top right panel, and one for deflector settings causing an offset along q_x of 0.65 a.u. (grey-scale intensity plot at the bottom right panel).

deflector voltages by 77 V. Indeed two peaks of roughly equal intensity are observed here, with the same binding energies as the peaks at $p_y = 0.65$ a.u. ($p_x = p_z = 0$). As the whole line along which we measure the SMD is now along the Brillouin zone edge a splitting is expected for all p_y values up to $p_y = 0.65$ where the edge of Brillouin zone 2 is reached.

4. Conclusion

We have shown how to check experimentally the alignment of a high-energy EMS spectrometer by verifying that the intensity of the outer valence band of Li_2O has indeed the lowest possible intensity at zero momentum. Moreover we showed, using a Si single crystal, that we can shift the line, along which the SMD is determined, in a controlled way along an arbitrary direction, validating the electron optics simulation of the deflectors, thus establishing that we can measure energy-resolved momentum densities along arbitrary lines in q -space.

Acknowledgements

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References

- [1] R. Camilloni, A.G. Guidoni, R. Tiribelli, G. Stefani, Coincidence measurement of quasifree scattering of 9 -keV electrons on K and L shells of carbon, *Phys. Rev. Lett.* 29 (1972) 618.
- [2] C. Gao, A.L. Ritter, J.R. Dennison, N.A.W. Holzwarth, Spectral momentum density of graphite from $(e,2e)$ spectroscopy: comparison with first-principle calculation, *Phys. Rev. B* 37 (1988) 3914–3923.
- [3] M. Vos, A.S. Kheifets, E. Weigold, F. Aryasetiawan, Clear evidence of electron correlation effects in the spectral momentum density of graphite, *Phys. Rev. B* 63 (2001) 033108.1–033108.4.
- [4] M. Vos, A.S. Kheifets, V.A. Sashin, E. Weigold, M. Usuda, F. Aryasetiawan, Quantitative measurement of the spectral function of aluminum and lithium by electron momentum spectroscopy, *Phys. Rev. B* 66 (2002) 155414.
- [5] M. Vos, G.P. Cornish, E. Weigold, A high-energy $(e,2e)$ spectrometer for the study of the spectral momentum density of materials, *Rev. Sci. Instrum.* 71 (2000) 3831–3840.
- [6] M. Vos, E. Weigold, Developments in the measurement of spectral momentum densities with $(e,2e)$ spectrometers, *J. Electron. Spectrosc. Relat. Phenom.* 112 (2000) 93–106.
- [7] M. Vos, S.A. Canney, D.R. Lun, E. Weigold, Determination of the anisotropic electronic structure of graphite by $(e,2e)$ spectroscopy, *J. Phys. IV* (9) (1999) Pr6-153.
- [8] M. Brunger, I. McCarthy, E. Weigold, High-resolution electron-momentum spectroscopy of argon: validation of technique and approximations, *Phys. Rev. A* 59 (1999) 1245.
- [9] V.A. Sashin, M. Vas, A.S. Kheifets, E. Weigold, High-resolution high-energy $(e2e)$ spectroscopy of metal oxides, in: L. Ancarani (Ed.), *Electron and Photon Impact Ionization and Related Topics 2002*, Institute of Physics, Bristol, 2003, pp. 79–88.
- [10] B. Soulé de Bas, H.E. Dorsett, M.J. Ford, The electronic structure of Be and BeO: benchmark EMS measurements and LCAO calculations, *J. Phys. Chem. Solids* 64 (2003) 495–505.
- [11] E.A. Mikajlo, K.L. Nixon, M.J. Ford, Electron momentum spectroscopy and linear combination of atomic orbitals calculation of bulk Na_2O , *J. Phys.: Condens. Matter* 15 (2003) 2155.
- [12] A. Kheifets, V. Sashin, M. Vos, E. Weigold, F. Aryasetiawan, Spectral properties of quasiparticles in silicon: a test of many-body theory, *Phys. Rev. B* 68 (2003) 233205.