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Report on the thesis

Development of methods for analyzing photoemission of quasi-two-dimensional structures on the example of graphene and 4*f* systems

by Artem V. Tarasov (St. Petersburg State University)

The thesis presents an impressive amount of methodological advance in analysis of the angle-resolved photoelectron spectroscopy (ARPES) and X-ray photoelectron diffraction (XPD) experimental data informing the electronic and atomic structure of solid-state systems, respectively. Furthermore, these methods are illustrated by their application to two interesting and technologically promising classes of materials, graphene/noble metal interfaces and 4*f*-electron compounds.

Chapter 1 presents a survey of the literature in the field. It covers, first, principles and applications of X-ray photoelectron diffraction (XPD) which allows element-specific structural analysis of surfaces and interfaces. An extension of this technique to a more direct method of photoelectron holography is discussed. My only and minor point here is that the author might have compared the low-energy regime of XPD, sensitive to the short-range order, to the high-energy (Kikuchi-like) regime in the few-keV range, sensitive to the long-range order (see, for example, J. Phys. Soc. Japan **91** (2022) 091006). The author follows with a survey of various spectroscopic methods to probe surface magnetism, focusing on the magnetic dichroism with linearly and circularly polarised X-rays and its applications to the 4*f* electron shells. Finally, an introduction is given to the physics of graphene/transition-metal interfaces and of rare-earth (RE) intermetallics, the two classes of materials studied in the thesis. The literature survey is to the point and full enough. The only point which I was stumbling upon was the made-up acronyms such as '(П)ДТСРСП' or 'РНРРИ' that sounded to me quite awkward. I would go with the well-accepted international acronyms such as (S)EXAFS and RIXS, respectively.

Chapter 2 unfolds basic theoretical and experimental concepts of the methods used in the present work, which include, in addition to XPD, ARPES and low-energy electron diffraction (LEED). At this point, I would only like to comment on the reference to the Koopmans' theorem. This theorem (or the DFT analogue of it) actually states that the Hartree-Fock (or DFT) energy of the highest occupied electronic orbital is equal to its ionisation energy, and does not say anything about other orbitals. Their energies actually differ from the Hartree-Fock (DFT) ones, and the

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difference is the energy- and **k**-dependent complex self-energy. At the end of the Chapter, the author describes the underlying DFT calculations employing the Full-Potential Local-Orbital (FPLO) minimum-basis code and Full-Potential Linearized Augmented-Plane-Wave (FP-LAPW) code WIEN2k. Careful analysis of the pros and cons of these two methods allows the author to optimally apply them to the whole range of computational problems in the present work. My last concern to the Chapters 1 and 2, however minor, would be their internal consistency. There are several repetitions between them, for example, in the discussion of the XPD. Admittedly, though, the enormous amount of results compiled in this thesis as well as dissimilarity of the investigated materials make the ideal organisation of the text hardly possible. Finally, I wished that the Chapters 1 and 2 had been wrapped up with concluding remarks, similarly to the following Chapters 3 and 4.

Chapter 3 develops a theoretical approach to tailor the R-factor analysis, commonly used in LEED, to the XPD data analysis. This approach includes numerical procedures to subtract the primary electron wave contribution, estimate correlations between structural and non-structural parameters determined by minimization of the R-factor, etc. Here, I would only like to bring the author's attention to the normalisation of the experimental XPD images prior to further processing. The chosen normalisation to the X-ray incidence angle implies that the light footprint on the sample spreads out of the analyzer's field of view. With nowadays synchrotron-radiation sources, however, the footprint is normally <100 µm, which ensures that it stays well within the field of view of >2 mm, typical of the modern analyzers, for any realistic sample rotation angle. This fact eliminates any need to normalise the XPD images to the X-ray incidence angle (J. Synchr. Rad. **20** (2013) 517). The author then demonstrates a successful application of the R-factor analysis to the XPD data from $CeIrIn_5$ the intermetallic compound featuring CeIn and In surface terminations. The previously overlooked $\sqrt{2}\times\sqrt{2}\ R45^{o}$ reconstruction of the latter has been found, which prohibits formation of the Rashba-split surface states characteristic of the CeIn termination. Further on, the author works out a novel approach to the photoelectron holography, which naturally incorporates the backscattering and multiple scattering effects all neglected in the previous works. This approach is applied to the (B-doped) graphene/Co interfaces, potential materials for spintronics, in order to determine the top vs hollow positions of the B atoms relative to the Co substrate ones over two graphene sublattices.

Chapter 4 in its first part recaps theoretical methods to calculate photoemission from 4*f* electronic shells including the multiplet effects. These methods are then applied to calculate the spectra of trivalent lanthanides resolved in the M_J quantum number. As demonstrated for $TbRh_2Si_2$, the comparison of these spectra with the experiment informs the magnetic moments of the RE atoms over different atomic layers in the subsurface region. An advantage of this theory-based analysis of the magnetic dichroism is an implicit inclusion of the photoexcitation matrix elements which can significantly distort the dichroic photoemission response. In its second part, the Chapter presents modelling of XPD spectra from the 4*f* electrons applied to $EuIr_2Si_2$ for determination of the Eu^{2+} vs Eu^{3+} distribution, magnetic order and atomic relaxation across the layers at the Tb- and Si-terminated surfaces. Another methodological advance here is the analysis

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of XPD resolved in separate lines of the 4*f* multiplet, which can utilise their individual chemical shifts to achieve the layer resolution. Finally, the author demonstrates how the temperature dependence of the 4*f* multiplet can inform the crystal field in the subsurface region. In a near perspective, the developed methodology can be extended from crystalline surfaces to layered magnetic heterostructures for spintronics.

Overall, I am impressed by the amount, depth and novelty of the scientific knowledge achieved in this thesis. My critique remarks above shall be viewed merely as suggestions for further development of the apparently fruitful research work of the author. If these remarks might affect the general assessment of the thesis, it would only be about its standing between excellent and spectacular. The theoretical and methodological developments are convincing, the experimental dataset is solid and extensive, and the interpretations are reliable. As demonstrated for graphene- and RE-based interfacial and layered systems, the results of this thesis bear a significant potential for accurate determination of the crystallographic and electronic-structure parameters of novel electronic and spintronic materials using XPD and ARPES. The results of this work are reported in 5 publications in refereed journals. The thesis stands as a significant development in the field of condensed-matter physics, and Artem V. Tarasov the author undoubtedly deserves awarding him the degree of candidate of physical and mathematical sciences.

Sincerely,

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