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To:
Dr. Ivana Radosavljevic Evans
Senior Lecturer in Structural/Materials Chemistry & International Coordinator
Department of Chemistry
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Application for the PANalytical Thesis Prize for Physical Crystallography 2012

Thesis : Neutron and Resonant X-ray Scattering Studies of Low Dimensional Quantum Magnets, Department of Physics, University of Bristol

Dear Dr. Evans,

I am writing to apply for the PANalytical Thesis prize in Physical Crystallography.

For my thesis I have worked on several projects using the experimental techniques of resonant X-ray and elastic and inelastic neutron scattering to explore order and dynamics in low-dimensional quantum magnets. My main project focused on synchrotron X-ray measurements on the hexagonal metallic magnetic $AgNiO_2$ to explore the spontaneous transition below 365 K to a supercell crystal structure with a periodic arrangement of expanded and contracted NiO_6 octahedra. The electronic energy levels of the Ni sites were probed by varying the X-ray energy through the Ni K-edge resonance (1s->4p) and a large enhancement of the supercell peak intensity was observed. I developed an empirical model for the anomalous atomic scattering factors to account quantitatively for all feature observed in the rich spectral lineshapes (in absolute units) taking into account Kramers-Kronig relations between real and imaginary parts and a full modelling of the energy-dependent absorption effects. The empirically extracted form factors showed an energy shift of 2.5 eV in the resonance energy for the different Ni sites. Comparison with LDA calculations that included the quantitative shifts in the 4p-levels due to the structural hybridization with the surrounding oxygens, indicated a large contribution to the resonance energy shift due to a change in the 1s core level, a characteristic signature of different number of electrons between the crystallographically distinct Ni sites. Measurements thus provided the first direct experimental evidence for spontaneous honeycomb charge order in the triangular Ni lattice and gave support to a recently developed theoretical proposal that charge order can be an energetically more favourable ground state to lift the orbital degeneracy in systems near the Mott transition, as opposed to the conventional Jahn-Teller orbital order found in more insulating systems.

This project required me to develop new tools for quantitative analysis of resonant xray scattering data for Physical Crystallography studies well beyond the currently available tools. In particular I developed new methods for performing quantitative fits to the energy-dependent profiles and

extracting empirically the full energy-dependence of the atomic scattering factors modelling simultaneously the absorption corrections taking into account a complex sample shape and including the full complex form of the anomalous atomic scattering factors with Kramers Kronig relation between the real and imaginary parts.

The results of this project have been published in 2011 in Physical Review Letters where I am first author and this work has been selected for one of the Science Highlights in the Annual Report of the Diamond Light Source. My thesis has been nominated for a commendation in the School of Physics at the University of Bristol. I have given oral presentations on the resonant X-ray results at the "Symposium on Quantum Materials" in Oxford, May 2011 and also at the summer school REXS2011 "Resonant Elastic X-ray Scattering in condensed matter", Aussois, France in June 2011.

Thank you for considering me for the PANalytical Thesis prize in Physical Crystallography.

Sincerely yours,

Lucian Pascut

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