considerable number of least-squares parameters could be omitted. Recent efforts have shown that this could indeed be a feasible approach [2]. We are currently investigating how ADPs can be calculated efficiently *via* cluster calculations. A suitable approach appears to be the ONIOM method [3], where a quantum chemical calculation is split into a high-level and a low-level part. ONIOM calculations allow geometry optimizations of a central molecule in a cluster of surrounding molecules as found in the crystal lattice. A C-program to generate input clusters for use with the GAUSSIAN program [4] was coded. We have performed a series of calculations treating a central molecule of interest with various high-level basis sets, and the surrounding layer of molecules with the UFF force field or various other lower-level quantum chemical approximations. Input geometries from invariom refinement [5] are suitably accurate to grant successful optimizations, and we find that accurate H-atom positions are crucial for convergence. It has already been shown that the 'internal' modes of hydrogen-atom vibrations can indeed be predicted from such calculations [6]. The next step, obtaining all-atom vibrational frequencies that can be converted to ADPs, requires a realistic description of the interaction between central and surrounding molecules in the cluster. To benchmark the calculated ADPs we attempt to predict the temperature dependence of ADPs. A number of amino-acid structures are studied where both high-quality low- or multi-temperature X-ray data, but also room-temperature ADPs from neutron diffraction are available. A by-product of these efforts are *temperature-dependent* ratios between the Uiso of riding H- and the respective parent atom. Their inclusion would be beneficial for crystallographic refinements with constrained hydrogen atoms based on low-temperature data. Despite the fact that the R-factor is rather insensitive to H-atom scattering in general, these ratios are more realistic than the fixed values for room temperature data currently in use.

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**Keywords: *ab-initio* calculations, charge density, atomic displacement parameters**

## FA3-MS20-T04

**Spin and magnetization density in the kagome staircase system $Co_3V_2O_8$.** N. Qureshi[a], M. Zbiri[b], H. Fuess[c], H. Ehrenberg[d], Y. Sakurai[e], M. Itou[e]. [a]*University of Cologne, Institute of Physics II, Germany.* [b]*Institut Laue Langevin, Grenoble, France.* [c]*Materials Science, Technical University Darmstadt, Germany.* [d]*Institute for Complex Materials, IFW Dresden, Germany.* [e]*Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, Japan.*
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$Co_3V_2O_8$ represents the 3$d$ transition metal ortho-oxo vanadates labeled as kagome staircase structures and crystallizes in the orthorhombic space group Cmca [1]. Its crystal structure is characterized by edge-sharing $CoO_6$ octahedra forming buckled layers of corner-sharing triangles, the kagome staircases, which are separated along the $b$ axis by $VO_4$ tetrahedra. In contrast to the ideal kagome net the geometric frustration is relieved due to two inequivalent Co sites ($Co_c$ *cross-tie* on 4a sites, $Co_s$ *spine* on 8e sites) and slightly different Co-Co bond lengths. The magnetic coupling is effectuated via a 90° Co-O-Co superexchange pathway. The ferromagnetic ground state reveals two strongly different magnetic moments for the $Co_c$ and $Co_s$ of 1.54 $\mu_B$ and 2.73 $\mu_B$, respectively [2], despite the fact that both $Co^{2+}$ ions apparently present high-spin configurations as macroscopic measurements exhibit saturation of the *cross-tie* moments [3]. Investigating the magnetization density may reveal preferred superexchange pathways with the presence of magnetization on the involved O sites. Eventual induced magnetization on the empty $d$-shell of V sites would allow interlayer coupling by super-superexchange. Therefore, magnetic Compton scattering and polarized neutron diffraction experiments have been carried out leading to the spin density in momentum space and the magnetization density in real space, respectively. *Ab initio* wave functions have been derived by hybrid DFT-based quantum chemical cluster calculations for the two different $CoO_6$ clusters. The resulting molecular orbitals have been used to build up a theoretical model able to be refined to the real and momentum space quantities at the same time.

Our results give the first reasonable explanation for the strongly reduced $Co_c$ moment in this system, which is not due to competing magnetic interactions, but a consequence of the covalent character of the $Co_c$ ion.

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## FA3-MS20-T05

**Time-resolved X-ray diffraction study of the piezoelectric response of single crystals.** Raphael Grifone[a], Oleg Schmidt[a], Semen Gorfman[b], Ullrich Pietsch[a]. [a]*Solide State Physics, University of Siegen, Siegen, Germany.* [b]*Department of Physics, University of Warwick, Coventry, UK.*
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The atomistic origin of the physical properties of solids such as dielectricity and piezoelectricity can be understood on the basis of precise investigations of the atomic movements induced by an applied electric field. In our previous studies we investigated the bond-selective response of $Li_2SO_4 \cdot H_2O$ [1] and GaAs [2] single crystals to a quasi-static external electric field. In order to generate dynamical processes in a crystal we developed special electronic circuits allowing for fast ( down to 200 ns) switching of electric, between four states of high voltage (HV), $U_+$, $U_0$, $U_+$, $U_0$, applied periodically to thin plane-parallel crystal plates. The frequency of the applied HV can be adjusted between 1Hz and 10 kHz, so that we were able to perform the experiment at a resonance frequency of the crystal plate. The time-dependent dynamical crystal response was studied by measuring the ω-rocking curves of a few Bragg reflections. Minimum time resolution of 20ns was achieved

based on a special FPGA based data acquisition system. Sufficient counting statistics was realized by summing up over about $10^6$ succeeding HV cycles for each $\omega$-angle of a rocking curve.

The experiments at piezoelectrical GaAs and $Li_2SO_4.H_2O$ crystals have been performed at BM01A (Swiss-Norwegian) beamline @ ESRF using a KUMA 4-circle goniometer and an open point detector. The 250$\mu$m thick (111) GaAs sample was sandwiched between 500nm insulating $SiO_2$ layer on both faces to avoid a current flow through the crystal. The HV was applied via thin gold-chromium contacts exactly sputtered on top of each other. At $Li_2SO_4.H_2O$ the longitudinal piezoelectric effect was found to be 10 times larger compared to GaAs. As main result of fast switching of HV we observed an oscillation of the angular position of the Bragg peak, with the oscillation frequency correlated to certain eigenmodes of the crystal plate. The amplitude of the oscillations depends on the magnitude of piezoelectric and elastic modulus, i.e. it is higher for $Li_2SO_4.H_2O$ compared to GaAs. On the other hand we did not observe such oscillation of the integrated intensities which can be interpreted by the fact that internal redistribution of atomic positions due to the oscillations of the lattice constants is negligible.

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