Frustration in transition metal compounds

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The interest in frustrated magnetism experienced a tremendous boost in recent decades due to its relevance for a plethora of highly exciting topics like high-temperature superconducting (HTSC) cuprates, type-II multiferroics or spin liquid states etc. A complementary approach to studying the HTSC cuprates directly is to study isostructural reference systems. We observed signatures of frustration in the isostructural cobalt and nickel oxides which arises from a phenomenon that we call "nano phase separation" and which is also able to explain the magnetic excitation spectra in these systems. One of our findings for the other aforementioned topics is the discovery of a new type-II multiferroic material - Cu_2OCl_2 - where frustration creates a cycloidal magnetic structure which in turn is responsible for the ferroelectric properties.

Frustrated magnetism is a very active research field in solid state physics. In a magnetic system geometric frustration hampers the formation of simple antiferromagnetic ground states at low temperature and enables the discovery of new states of matter like spin liquids. Also in several of the recently discovered type-II multiferroic materials frustration plays a decisive role. In such materials spiral magnetic structures might emerge due to frustration and ferroelectricity appears e.g. according to the inverse Dzyaloshinskii-Moriya interaction mechanism. Moreover, even in the high HTSC cuprates $La_{2-x}Sr_xCuO_4$ with K_2NiF_4 (2-1-4) structure frustration might play a relevant role since it might explain the (incommensurate) magnetism in the lower hole-doped regime. Recently our group proposed a novel nano phase separation scenario for the isostructural cobaltates $La_{2-x}Sr_xCoO_4$ which could point to the relevance of frustration for the so-called hour-glass magnetic spectrum that is ubiquitous for the HTSC cuprates and that was also observed in the isostructural 2-1-4 cobaltates. Thus, frustration is linking some of the most active research fields in contemporary condensed matter physics.

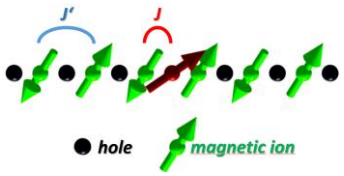

Fig. 1: Schematic visualization how frustration is introduced into a checkerboard charge ordered system (here only one chain of ions is shown; the perpendicular chain behaves correspondingly). The magnetic ions are coupled via an antiferromagnetic exchange interaction J' across the non-magnetic holes. Once a charge is doped on a hole (red sphere) a very strong exchange interaction $|J| >> |J'|$ is introduced into the system that wants to align the surrounding spins in an antiparallel manner. This causes frustration in the system.

Spin excitations in 2-1-4 cobaltates & nickelates

Magnetic interactions might play an important role for the superconducting pairing mechanism in cuprate high-temperature superconductors (HTSC). An ubiquitous property of most of the HTSC cuprate materials is the appearance of a magnetic excitation spectrum that resembles an hour-glass if plotted in energy-momentum space. Either Fermi surface effects or charge stripes might provide an explanation for these famous excitation spectra. However, even some of the most prominent features of these hour-glass spectra, like the suppression of the outwards-dispersing branches, are not yet well understood on a microscopic level. Recently, we proposed an alternative nano phase separation scenario that could also explain the occurrence of hour-glass spectra in the isostructural cobaltates which are isostructural to the prototypical cuprates $La_{2-x}Sr_xCuO_4$. Our scenario (for cobaltates) is based on magnetic frustration that appears when undoped islands (with strong nearest neighbor exchange interactions *J*) are doped into a checkerboard charge ordered matrix (with weaker exchange interactions *J'* across a hole), see Fig. 1.

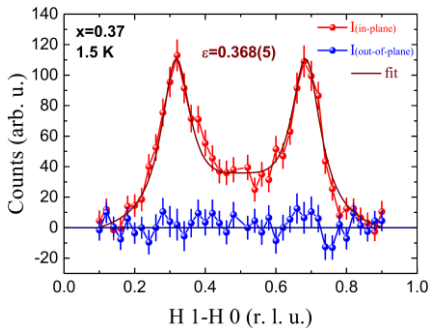

Fig. 2: Magnetic signal in $La_{1.63}Sr_{0.37}CoO_4$ observed with polarized neutrons. Clearly, magnetic intensities can be seen around H = 0.5 between the two incommensurate magnetic peaks [1].

In continuation of our earlier work [2, 3] we have grown $La_{2-x}Sr_xCoO_4$ single crystals in a wide range of hole-doping with the floating zone technique. X-ray absorption spectroscopy measurements confirm the oxygen stoichiometry of our $La_{1.63}Sr_{0.37}CoO_4$ single crystals. In a comprehensive study [1] comprising neutron, muon and X-ray experiments we were able to verify and better "quantify" our nano phase separation scenario which is the source of frustration.

Importantly, the magnetic signal that we re-analyzed with polarized neutrons exhibits intensities at half-integer positions in reciprocal space – see Fig. 2 – which were expected for nano phase separation [1]. These intensities are connected to the presence of undoped islands within the checkerboard charge ordered matrix and appear also in our numerical simulations for nano phase separation models.

Basically, the charge correlations in these cobaltates are governed by checkerboard charge ordering modulations of short range character resulting in rather broad signals at half-integer positions in reciprocal space that appear below ~800 K [1] and broaden with further decreasing temperature. This anomalous broadening could be either attributed to a small admixture of charge stripe ordering (of the order of ~10% appearing below room-temperature) or to an anomalous peak broadening of the broad checkerboard charge ordering signal which might originate from the freezing-in of disorder [1]. Subsequent X-ray photon correlation spectroscopy (XPCS) experiments reveal a slowly fluctuating character of these charge correlations with time-scales of the order of an hour [1]. The hole-doping dependence of the corresponding relaxation times τ are shown in Fig. 3. Interestingly, these correlation times extrapolate to zero for $x \rightarrow 0.32$. This value is about the value where the breakdown of incommensurate magnetism was observed for oxygen-stoichiometric $La_{2-x}Sr_xCoO_4$ samples and directly points to the relevance of checkerboard charge ordering correlations for the observation of incommensurate magnetism in the system.

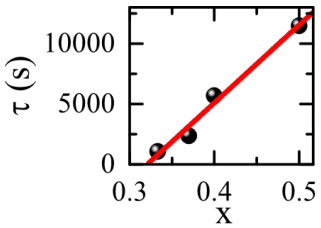

Fig. 3: Doping dependence of the relaxation time τ of the broad charge ordering signal around half-integer positions in reciprocal space [1].

We also re-analyzed the magnetic phase diagram by means of muon-spin relaxation (μSR) measurements [1]. Our magnetic samples show the highest ordering temperatures reported in literature and are not indicative for the occurrence of charge stripes below $x = ½$. Especially, the lower doped regime $0 < x < 0.4$ shows very high magnetic ordering temperatures that are starting from the very high values of $T_N \sim 275$ K for our undoped sample La_2CoO_4 and continuously decreasing towards higher hole-doping level x without any signs for anomalies in the lower doped regime (that was attributed in literature to the possible presence of charge stripes in the past but that could arise from ill-defined oxygen contents instead) – see Fig. 4.

All these observations are strongly in favor of a nano phase separation scenario which is mainly based on checkerboard charge ordered ("$La_{1.5}Sr_{0.5}CoO_4$-like") and undoped ("La_2CoO_4-like") regions. A small additional admixture of charge stripe ordered ("$La_{5/3}Sr_{1/3}NiO_4$-like") regions cannot be excluded but is not the dominating ordering scheme in these cobaltates.

Finally, the study of the magnetic excitations with temperature [1] shows that nano phase separation is

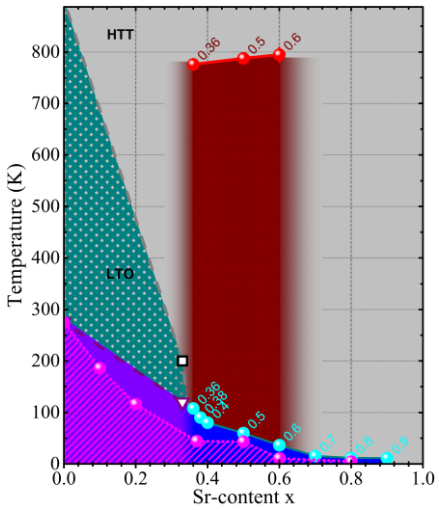

Fig. 4: The phase diagram of $La_{2-x}Sr_xCoO_4$ [1]. The magenta points indicate the magnetic ordering onset temperatures observed in our μSR measurements. (Cyan data points were observed in complementary neutron scattering experiments that are probing a different time scale.) A gradual decrease with hole-doping x can be observed. The red data points indicate the onset of checkerboard charge ordering.

distinct from conventional phase separation where one would expect a kind of superposition of the magnetic excitation spectra of $La_{1.5}Sr_{0.5}CoO_4$ and La_2CoO_4 (including their different temperature-dependence). That this was not the case in our $La_{2-x}Sr_xCoO_4$ samples shows that the two regions involved in nano phase separation are strongly interacting and forming a single system (like a cluster spin glass phase) and not two well-separated magnetic phases as would be expected for conventional phase separation. Interestingly, our nano phase separation scenario also provides a nice picture for the suppression of the outwards dispersing branches of hour-glass spectra because it naturally explains a difference between both kinds of branches within these spectra [1].

A second 2-1-4 system that attracted our attention was the nickelate system RSrNiO$_4$ (R = La, Nd, Y) which is also isostructural to the prototypical HTSC cuprate materials. Using a high pressure mirror furnace we have grown cm-sized RSrNiO$_4$ single crystals [4]. X-ray absorption spectroscopy measurements confirmed the Ni^{3+} valence of our NdSrNiO$_4$ single crystals. Neutron measurements indicate the presence of roughly quarter-integer magnetic peaks and a magnetic excitation spectrum with a steep upwards dispersion [4]. Our interpretation of the data is that charge disproportionation occurs in this Ni^{3+} system which would naturally explain the almost quarter-integer magnetic reflections. Using again a nano phase separation model, the small incommensurability can be explained since frustration naturally appears in this scenario. And also the magnetic excitation spectrum is consistent with such a model, see Fig. 5 [4].

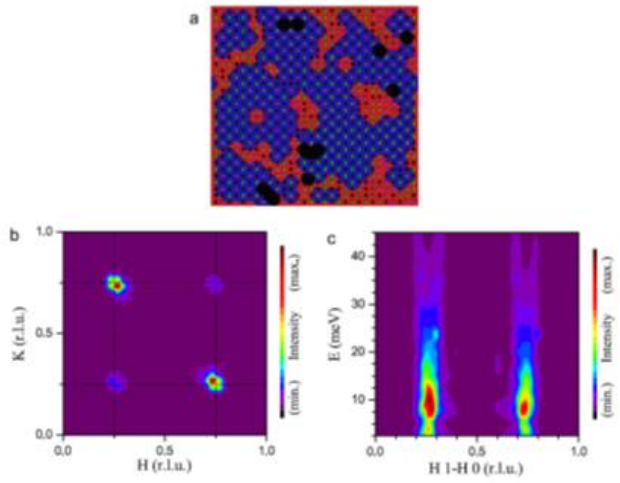

*Fig. 5: Spin wave simulations of $RSrNiO_4$ within a nano phase separation scenario [4]. In **a** one of the four 30 × 30 meshes obtained from Monte-Carlo simulations is shown. In **b** and **c** the calculated elastic and inelastic neutron scattering intensities are shown which strongly resemble the experimental observations.*

Hence, frustration which appears within a nano phase separation scenario could play an important role in 2-1-4 nickelates and cobaltates which are isostructural reference systems for the prototypical HTSC materials.

Multiferroicity in Oxychlorides

Multiferroic materials attracted enormous interest in recent decades triggered by key findings as the observation of magnetically induced ferroelectricity in $TbMnO_3$ that comes along with sizeable magneto-electric effects in these so-called type-II multiferroic materials. In some cases, frustration is the driving force for a non-collinear magnetic structure that is responsible for the ferroelectric properties. E.g. in systems with cycloidal magnetic structure the polarization P can be understood by the inverse Dzyaloshinskii-Moriya interaction mechanism.

Recently we observed dielectric anomalies and the occurrence of a pyroelectric current at T_N in an oxychloride – Cu_2OCl_2 (melanothallite) [5]. Regarding the magnetic ions the melanothallite crystal structure resembles the pyrochlore structure. Hence, a high degree of frustration can be expected in this system.

In continuation of our previous work we were now able to confirm the multiferroic properties of copper oxychloride by revealing a hysteresis within P-E-loop measurements which disappears at $T_N \sim 70$ K, see Fig. 6 [6]. Moreover, we co-aligned about a dozen Cu_2OCl_2 single crystals and made use of polarized neutrons for

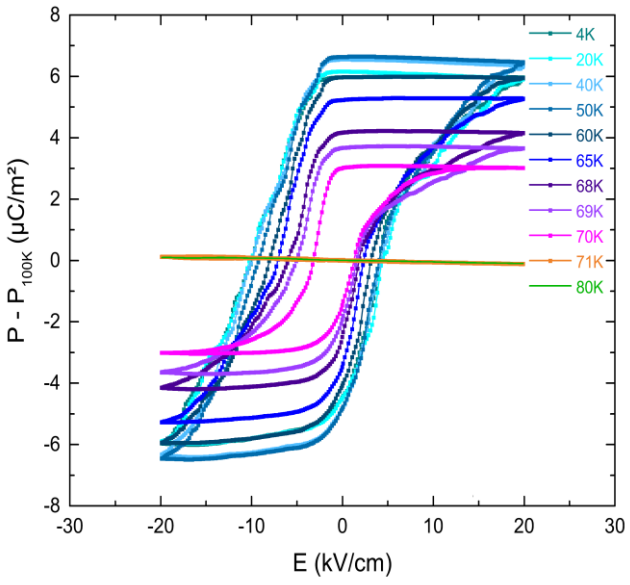

Fig. 6: P-E hysteresis loops of Cu_2OCl_2. The hysteresis disappears exactly at $T_N \sim 70$ K [6].

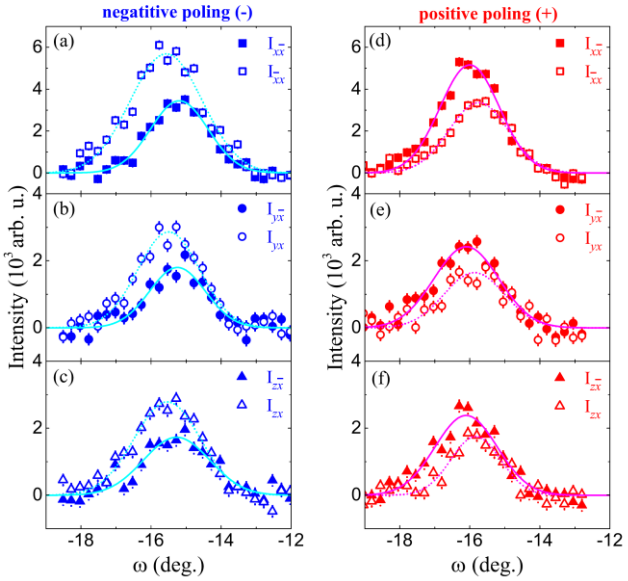

Fig. 7: Polarized neutron diffraction intensities measured at ~2K on the (−1.17 2 0) magnetic reflection after (a–c) a positive electric poling and (d–f) a negative electric poling of the single crystal [6].

showing that the so-called chiral term r_{chir} of the magnetic neutron scattering intensities (Blume-Maleev equations; $r_{chir} = (I_{x\bar{x}}-I_{\bar{x}x})/(I_{x\bar{x}}+I_{\bar{x}x})$) depends on the electric poling of the sample, see Fig. 7. I.e. the vector chirality can be reversed by the application of an external electric field, as the relative intensity of $I_{x\bar{x}}$ and $I_{\bar{x}x}$ can be reversed by an opposite poling of the sample [6].

All these observations reveal the emergence of spin-induced ferroelectricity in Cu_2OCl_2, thus showing that copper oxychloride is a type-II multiferroic material with quite high critical temperature of ~70 K [6]. Finally, we were able to solve the magnetic structure of this novel multiferroic material by means of single crystal (and powder) neutron diffraction. It turns out that copper oxychloride has a cycloidal spin structure with moments spiraling in the *ac* plane, see Fig. 8. The

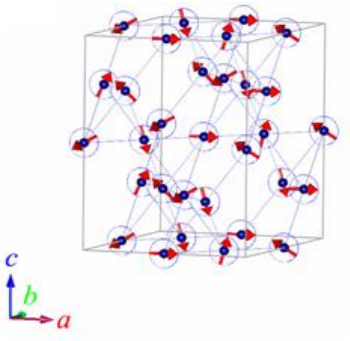

Fig. 8: Magnetic structure of Cu_2OCl_2 [6].

electric polarization $P \propto e_{ij}\times(S_i\times S_j)$ that can be calculated for this magnetic structure according to the inverse Dzyaloshinskii-Moriya interaction mechanism is non-zero and additionally also points in *c*-direction which is exactly the same direction as observed experimentally [6]. Finally, a cycloidal magnetic structure induced by frustration turns out to be the driving force of multiferroicity in Cu_2OCl_2.

New systems with frustration

We also searched for new materials with geometric frustration and were able to identify e.g. $Ba_{26}Ru_{12}O_{57}$ as such kind of material [7]. Currently, we are examining the physical properties of $Ba_{26}Ru_{12}O_{57}$.

External Cooperation Partners

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