Office of Science Graduate Student Research

2022 Solicitation 2 - Mid-Award Report for: Tyler Chase Sterling

Awardee and Project Information

Awardee Name:	Tyler Chase Sterling
Graduate Institution:	University of Colorado Boulder
Discipline:	Condensed Matter
Doctoral Dissertation/Thesis Title:	Physics of Energy Materials Investigated by Neutron Scattering
Degree Objective:	Ph.D.
Expected Graduation Date:	12/2024
SCGSR Research Project Title:	Probing the Non-Equilibrium Process of Electroluminescence Via in situ Neutron Diffuse Scattering
SCGSR Research Project Abstract:	It was recently demonstrated that application of a moderate electric field at elevated temperatures modifies materials' structural, electrical, optical, and other properties turning them effectively into new materials. When the field is applied and the material is heated above room temperature very briefly, its electrical conductivity increases dramatically and it begins to glow in an electroluminescence (EL) like phenomenon described as "flash." The physical mechanisms behind this process and the properties of the new materials that it creates are not understood. Even more puzzling, it was recently shown that applying a magnetic field to a sample undergoing EL causes nearby materials to EL too. We propose to perform in situ neutron diffuse scattering (NDS) experiments under simultaneous electric and magnetic fields. An apparatus for in situ electric field experiments already exists and we have used it to prove that in situ NDS can be used to probe the EL state. We plan to modify the apparatus to work under simultaneous electric and magnetic fields. We will apply these new tools to a technologically important class of materials: relaxors. The first step will be to solve for the response of the local atomic order to applied fields. Then we will develop computational models for the non-equilibrium many body processes involved in EL.
Starting Date:	6/12/2023
Ending Date:	5/31/2024
Host DOE Laboratory:	Oak Ridge National Laboratory (ORNL)
Division at the Host DOE Laboratory:	Neutron Scattering Division
Collaborating DOE Laboratory Scientist Name:	Feng Ye
Collaborating DOE Laboratory Scientist Email:	yef1@ornl.gov
Supervisor for Collaborating DOE Laboratory Scientist:	N/A
Scientific user facility involved in the SCGSR research project:	Spallation Neutron Source (SNS)

Research Goals and Objectives	
Research Goals and Objectives:	It was recently demonstrated that application of a moderate electric field at elevated temperatures modifies materials' structural, electrical, optical, and other properties turning them effectively into new materials. When the field is applied and the material is heated above room temperature very briefly, its electrical conductivity increases dramatically and it begins to glow in an electroluminescence (EL) like phenomenon described as "flash." The physical mechanisms behind this process and the properties of the new materials that it creates are not understood. Even more puzzling, it was recently shown that applying a magnetic field to a sample undergoing EL causes nearby materials to EL too. The main challenges in this field are to understand the underlying microscopic mechanism and to learn how to harness it to create new materials.

We proposed to perform in situ neutron diffuse scattering (NDS) experiments under simultaneous electric and magnetic field. An apparatus for in situ electric field experiments already exists and we have used it to prove that in situ NDS can be used to probe the EL state; we have data on rutile TiO_2 from in situ and ex situ NDS experiments that are shedding light on the physics of flash. As follow up work, we proposed to perform in situ NDS experiments on relaxor ferroelectric PMN-PT. The measurements were planned for the beginning of the fellowship and were completed without delay. We were not only able to measure relaxor PMN-PT but also rutile TiO_2 under different flash conditions and perovskite $SrTiO_3$. We are still working on data analysis and understanding the structural changes to the crystals: NDS datasets are huge and difficult to analyze. We have developed some custom computational tools for the analysis and some other tools are needed and planned (section 'Total Diffuse Scattering' in 'Additional Materials').

We also plan to use our knowledge on what happens structurally to develop a many-body model for the physics of EL. However, we first need to understand the microscopic structural changes. Modeling the physics remains a "next-step".

Finally, we have performed other unplanned materials properties measurements to learn how flash affects the materials' properties and how we can use flash to control properties to create new materials. Specifically, we have measured resistivity and magnetization as a function of temperature for flashed vs. pristine rutile TiO_2 and shown that flash has a pronounced effect. What the effect is and its implications are under investigation. We have also provided flashed samples of rutile TiO_2 and $SrTiO_3$ to a collaborator who can detect superconductivity with very high sensitivity. Doped $SrTiO_3$ is known to be superconducting and we want to see if flash has changed the transition temperature or other properties in some way. Pristine TiO_2 is not superconducting (it's an insulator) but flashed TiO_2 is conducting and we want to see if it superconducts. We are waiting on the results. |

Project Accomplishments:

In situ NDS experiments under electric field were completed successfully (we did not measure under magnetic field; see below). Not only did we measure PMN-PT, but we also measured another rutile TiO2 crystal with current along a different crystal axis as well as perovskite SrTiO3. Each of these samples was measured in situ and ex situ; samples were measured under flash with numerous current densities and then the flashed samples were measured ex situ without a furnace or electrodes in the sample environment. We also attempted to measure high-Tc superconductor La2CuO4 in situ but the sample broke and we didn't have spares. The results of these experiments are discussed below.

TiO2 is tetragonal with the a and b axes equivalent. Previous experiments on rutile TiO2 were done with current along the a axis. From the previous measurements, we are primarily using data from a sample that was flashed in air at CU boulder and then quenched in liquid nitrogen to freeze in defects. We are focusing on these data because the in situ data have an enormous background due to scattering of neutrons from the sample environment (furnace, sample stick, electrical leads, etc.). The ex situ data are very clean by comparison. The data show pronounced scattering that indicates formation of oxygen vacancies that order into parallel planes; this phase resembles the known Magneli phase of reduced TiO2. The in situ data show the same features, but the data are hard to quantify due to the background.

Interestingly, the new experiments mentioned above (with current along the c axis) show both the signature of the Magneli phase as well as new features that we can't link to a known phase of reduced TiO2. Whether or not the new NDS features are due to the change in current direction remains to be proven; there are other differences in experimental conditions that need considered. The data we are using from previous experiments used a crystal that was flashed in air and then quenched in liquid nitrogen to freeze in defects. The new data set (with current along c-axis) is from a crystal that was flashed in vacuum and then removed and measured ex situ. As such, it is difficult to claim whether or not the new features are from the current direction dependence, vacuum vs. air, etc.

We suspect the effect of vacuum is to enhance the rate at which oxygen leaves the crystal. This claim is based on the following observations: heating a TiO2 crystal is known reduce it. The heat mobilizes oxygen defects that diffuse out of the crystal (the crystal reduces). Reduced crystals become more conducting and less optically transparent (Figure. 3 in 'Additional Materials'). The opacity is correlated with the amount the crystal is reduced. The observation we made is that crystals flashed in vacuum are much more opaque than crystals flashed in air. This is true for TiO2 as well as PMN-PT and SrTiO3. It is also known that oxygen vacancies are charged (analogously to a positively charged electron hole). The effect of the field is to drive the oxygen vacancies to move within the crystal. The behavior of the vacancies under different current densities and time under flash could then have an effect on the diffuse scattering. Unfortunately the phase space for these experiments (temperature, vacuum vs. air vs. inert gas. vs. reactive gas, current density, etc.) is enormous and neutron beam time is a highly limited resource. It is unfeasible to do enough neutron scattering experiments to disentangle these effects; rather, we plan to use different methods in the future (see 'Remaining Plans').

The results of scattering from PMN-PT and SrTiO3 are more cryptic. NDS from both crystals shows no readily observable change from scattering from pristine samples (which we also measured). PMN-PT is already known to show interesting diffuse scattering that is related to the so called "short ranged polar order". The features of this scattering are present in both the pristine and flashed crystal. The scattering from polar order is known to respond to electric field; careful analysis is needed to determine if the response of polar order is different under flash. Unfortunately, the furnace background masks these features and ex-situ experiments on PMN-PT cannot include in situ response to field (obviously). Analysis of these data is ongoing.

An interesting observation is that the opacity of PMN-PT crystals barely changes under flash (Figure. 3 in 'Additional Materials'). The pristine crystal is transparent, while the flashed crystals are still transparent but slightly gray. This is in contrast to TiO2 and SrTiO3 where the flashed crystals are black and opaque. Similar to PMN-PT, NDS from SrTiO3 shows no change from the pristine sample. Unlike PMN-PT, flashed SrTiO3 is black and conducting whereas the pristine crystal is transparent and insulating (Figure. 3 in 'Additional Materials').

The lack of diffuse scattering from SrTiO3 and PMN-PT is not necessarily a null result. Neutron scattering is a bulk-probe; neutrons scatter weakly from atoms, so penetrate deep into the crystal before scattering. It is possible that any oxygen vacancies that form in PMN-PT and SrTiO3 form near the surface. Any ordering near the surface of the crystal would not be visible in neutron scattering. The lack of diffuse scattering features from these samples doesn't necessarily mean there is no affect during flash. Clearly the flash process drastically changes the properties of SrTiO3 and, to a lesser extent, PMN-PT. The nature of these changes will require investigation with other methods (see 'Remaining Plans').

We were unable to build an apparatus to apply magnetic for in-situ NDS due to technical constraints; i.e. designing and manufacting the in-situ apparatus was going to be challenging and expensive. We decided not to pursue this now as we suspect that the real effect of the magnetic field is simply to heat the sample so much that it incandesces; i.e. the coil that produces the magnetic field is Joule-heated and heats the sample, which in turn incandesces rather than "flashes". Fellow group members at CU are building an experimental setup to test this; they will apply magnetic field to a crystal and measure resistance of the sample. At the onset of flash, there is a sharp drop in resistance, where as heating a normal semiconductor results in a gradual drop in resistance. Measuring the resistance under magnetic field will convince of us whether the magnetic field is relevant. If so, we will commission a capable sample environment and attempt more NDS experiments under magnetic field in the future.

We also attempted an in situ *inelastic* experiment on the ARCS spectrometer using the already available in situ sample apparatus; unfortunately some of the hardware at ARCS (the radial collimator) malfunctioned and the experiment was unsuccessful (see 'Additional Materials' for a detailed explanation, especially Figure 1). We are still convinced that the inelastic scattering will provide critical information about flash. Why? Briefly, neutrons inelastically scatter from a crystal by creating/absorbing lattice vibrations. The probability of scattering from a lattice vibration is related to the amplitude of that particular vibration in the crystal. In equilibrium, the ratio of probabilities of absorbing vs. creating a vibration follows the Bose-Einstein distribution. The goal of the inelastic experiment was to measure the ratio of creation vs. absorption. If the electric field is driving a particular lattice vibrational mode, this

ratio will be different from the Bose-Einstein distribution, signaling a non-equilibrium effect. The SNS (where ARCS is located) is now down for upgrades, so we plan to do analogous measurements on the triple-axis-spectrometer at HFIR. This requires a new sample environment; the engineers at SNS have already designed it and my advisor Dmitry Reznik has commissioned it to be manufactured. It should be completed by the end of January 2024 and we plan to do experiments soon after. Furthermore, when the SNS reopens, we plan to submit a proposal to re-try the ARCS experiment.

Some other miscellaneous accomplishments are worth mentioning: (i) We have developed software tools to aid analysis of NDS data. In a typical NDS dataset, the 'intensity' lies on a regular, rectilinear 3D grid in reciprocal space. In flashed TiO_2, the diffuse scattering features point along directions that are not commensurate with this grid. To quantify the size and shape of the diffuse scattering, we need to take 'line-cuts' (1D cuts plotting the intensity along a path through reciprocal space) along these arbitrary directions. For various reasons, existing tools that manipulate and post process NDS data cannot do this. We have developed an algorithm and program to do these cuts and this capability has proved essential to our analysis.

(ii) We have measured or are in the process of measuring physical properties of samples modified by flash. We have measured magnetization and resistivity of rutile TiO_2 modified by flash and compared to pristine TiO_2. There is a pronounced effect. The nature of the effect and its implication is still under investigation, but preliminary analysis suggests that the flashed crystal forms a charge-ordered state at low-temperature, frustrating the sample from becoming metallic. These measurements were carried out by collaborators at CU. We have also sent flashed $SrTiO_3$ and flashed rutile TiO_2 crystals to a collaborator to check for superconductivity. They can detect even small volumes of superconductors within an otherwise metallic crystal. $SrTiO_3$ is known to superconduct at low-T; we want to see if flash has modified the transition temperature of other properties somehow. Reduced TiO_2 is not known to superconduct, but we are interested to see if flash has changed this.

Uploading Additional Materials

Would you like to upload any additional materials?	Yes
Additional Materials:	SCGSR_mid_progress.pdf

Use of DOE Laboratory Resources

DOE Laboratory Facilities and Research Capabilities:	The use of DOE resources has been essential to my fellowship progress. All of the neutron scattering work carried during this fellowship was done at the SNS at ORNL, specifically the CORELLI and ARCS instruments. Additionally, we used the SNS user laboratory to prepare samples, i.e. to cut and align crystals. In the remainder of the fellowship, we will do experiments at HFIR. For the data analysis, we have depended heavily on computing resources at the SNS.

Remaining Plans

What do you plan to do for the remaining period of your SCGSR project until the ending date to accomplish the goals and objectives?	The primary goals to achieve in the remainder of the fellowship are as follows. (i) Finish data analysis. We have a large amount of data to analyze and a paper explaining the results in rutile TiO_2 is underway. This was intended to be finished earlier in the fellowship, but the new experiments on rutile TiO_2 are being included in the write up. Publishing the results on PMN-PT and $SrTiO_3$ will require more analysis as the data do not show interesting diffuse scattering (see 'Project Accomplishments' section).
	(ii) Complete inelastic scattering measurements. We attempted an inelastic scattering experiment at ARCS, but it was unsuccessful due to hardware problems (see 'What is a collimator?' section in 'Additional Materials'). The SNS is down for upgrades, so we plan to do analgous experiments on the triple-axis spectrometer at HFIR. A new sample environment is currently being manufactured for these experiments and the HFIR experiments are planned for early 2024.
	(iii) We want to analyze the total diffuse scattering results. Total diffuse scattering contains contributions from phonons and these data may show differences between flashed and pristine crystals where elastic diffuse data (called simply "NDS" above) do not. However, there are significant issues with the interpretation of neutron total diffuse scattering. See sec. 'Total diffuse scattering' in the 'Additional Materials' for more details. We summarize the issue here. For technical reasons, the instrument assumes that all scattering during the measurement is elastic. The scattering angle can be determined by tracking which detector the neutron hits. However, the change in momentum of the neutron is implicitly fixed by the assumption of elastic scattering. The result is that intensity is assigned to a different momentum bin than it physically belongs in. This is wrong. Moreover, the error depends on the scattering geometry, which differs from experiment to experiment. Therefore comparing different total diffuse scattering data sets and, in particular, comparing to total diffuse scattering calculations is difficult. Features that look interesting but are trivial may show up. Rather than correct the experimental datasets (which is impossible after-the-fact), we have devised an algorithm to calculate total diffuse scattering assuming elastic scattering so that the theoretical data are assigned to the same wrong bins as the experimental data. This method should allow us to identify anomalies, at least in the case where calculations are able to faithfully model the phonons. This algorithm is detailed in sec. 'Total diffuse scattering' in the 'Additional Materials'.
	These primary projects still require substantial work and will maintain my focus for the duration of the fellowship.
	Lastly, we are thinking beyond the duration of the fellowship. As valuable as the work we have done so far has been, we have also found opportunities for future work.
	We want to understand the nature of defects in e.g. $SrTiO_3$ where we suspect that there is ordering near the surface of the crystal. As discussed in 'Accomplishments', neutrons cannot see defects near the surface. Other methods, such as X-ray diffuse scattering (XDS) can. Unfortunately X-rays are not sensitive to low-atomic-number elements such as oxygen. If there is significant ordering in the Sr and Ti sub lattices due to flash, XDS will show it. On the other hand, if only the oxygen atoms are important, XDS will not be useful. This remains to be seen.
	Even further in the future (post-graduation), my advisor and I want to build a 'pipe-line' to systematically characterize flashed crystals in-house at CU Boulder. Our lab there has sophisticated Raman scattering capabilities and our collaborators across the hall have a PPMS to measure resistivity and magnetization. They are already helping us with rutile TiO_2. To prepare samples, we want to use a vacuum furnace that we will modify to allow flashing crystals under any atmosphere we choose, e.g. vacuum, intert gas, reactive gas (eg. oxygen), etc. We will be able to systematically explore phase space by simultaneously controlling temperature, current density, and atmosphere. Rather than using precious neutron scattering beam time, we will use Raman scattering and other methods to characterize the materials. This remains for the future.

Reporting Changes or Issues

Do you foresee any changes or issues in accomplishing the research goals and objectives?	No

Participation in Other Activities at the Host DOE Laboratory

Participation in research Seminars/Workshops within the division you are currently:	Occasionally
Participation in Research Seminars/Workshops in other divisions:	None
Participation in Training Seminars/Workshops on Professional Development:	None
Seminars/Workshops description:	

Reflection or Comments About Your Overall SCGSR Experience at the Host DOE Laboratory

Would you like to provide reflection or comments about your overall SCGSR experience at the Host DOE Laboratory?	No

Submit Date:	12/4/2023 3:24 PM

SCGSR mid-progress report: additional materials

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1   What is a radial collimator?

Neutrons scatter off the nuclie of atoms. The potential through which they interact is a "delta function": $V(\boldsymbol{r}) \sim b\delta(\boldsymbol{r} - \boldsymbol{R})$ where $\boldsymbol{r}$ is the neutron coordinate and $\boldsymbol{R}$ is the nuclear coordinate. b is the scattering length. In other words, the scattering is "point like"; i.e. the scattered neutrons radiate from a point. See fig. 1.

b is a small number and the crystal volume is usually small, so the probability of a neutron scattering off a crystal is low. The situation is worse if the sample environment includes e.g. a furnace; the furnace is large compared to the crystal, so the furnace will scatter a large fraction of the incident neutrons; any neutrons scattered from the furnace that hit the detector obscure scattering from the crystal. In other words, we don't care what the scattering from the furnace looks like. We call scattering from anything that isn't the crystal the "background". The background is undesirable. To minimize the background in an experiment with a furnace, we use a radial collimator (see fig. 1).

What is a radial collimator? The size of the sample relative to the distance to the detector is negligible, so scattering from different regions of the sample might as well be from the sample point. The scattered neutrons radiate "concentrically" (fig. 1 b). However, the furnace size is not negligibly small compared to the distance to the detector. Scattering from the furnace can happen at a position that is relatively far from the sample center. Neutrons scattered from the furnace are not concentric with scattering from the sample. We can use this fact to block neutrons scattered from the furnace. A radial collimator has slits that are aligned radially with the neutrons scattering from the sample (fig. 1 a); neutrons scattered from the sample will pass through. On the other hand, neutrons scattered from the furnace are not concentric with the collimator; they will be absorbed by it. In this situation, only neutrons scattered from the sample are detected and the background is minimal.

During our ARCS experiment, the collimator could not be moved into place. As such, we had to attempt the experiment without it. Without the collimator, however, all neutrons scattered from the furnace are detected and contribute to the background (fig. 1 b). In our experiment, the background was so large that we could see no scattering from crystal.
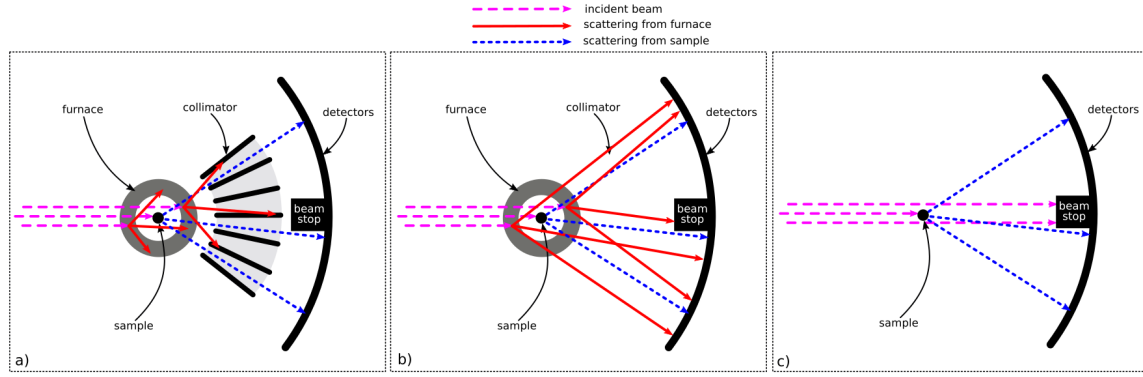
Fig. 1: Diagram showing a direct geometry scattering experiment (see fig. 2 below) with a furnace and collimator a), with a furnace and no collimator b), and without a furnace or collimator c).

2 Total diffuse scattering

Diffuse scattering measurements provide information about short ranged correlations and fluctuations in materials. Total diffuse scattering (TDS) measures all energy transfers, $E = E_i - E_f$, with E_i the energy of incident neutrons and E_f the energy of scattered neutrons. As such, TDS measurements provide information about both the *static* short ranged correlations and, since inelastic scattering is measured, the *excitations*: e.g. phonons. In an elastic diffuse scattering experiment, neutrons with $E_f \neq E_i$ are filtered out so that elastic scattering only measures static correlations.

Diffuse scattering is usually weak, so it imperative to optimize the experimental conditions for sensitivity to weak signal. I.e the advantage of TDS over elastic scattering is that no neutrons are filtered out; since no neutrons are wasted, there is greater intensity which means better statistics for a given amount of beam time. Of course, the intensity from excitations might be much stronger than the elastic scattering, so elastic diffuse scattering is still preferred in some circumstances.

TDS contains scattering from all energy transfers. Analyzing and histogramming the final energy of scattered neutrons is challenging technically. The easiest way to do it, e.g. what is done at ARCS, MERLIN, etc., is to use a monochromatic incident beam (i.e. all incident neutrons have the same energy, E_i) and record the time-of-flight. From this, the final speed, v_f, of the neutron can be deduced; the speed is directly related to the energy through $E_f = mv_f^2/2$, with m the mass of the neutron. These experiments allow us to measure the dispersion relation of excitations, i.e. $\omega(\boldsymbol{q})$.

Using a monochromatic beam requires filtering out neutrons. Monochromatic beams have lower flux than white beam and require much longer measurements to get reasonable statistics. For this reasons, TDS experiments on instruments like CORELLI use a white beam of incident neutrons: a white beam is thermal distribution of all incident energies. Unfortunately, with a white beam, it is impossible to deduce the energy transfer of the neutrons since, even if we measure the time-of-flight, we don't know the initial energy of a given neutron. An approximation has to be made when reducing the data from instrument coor-
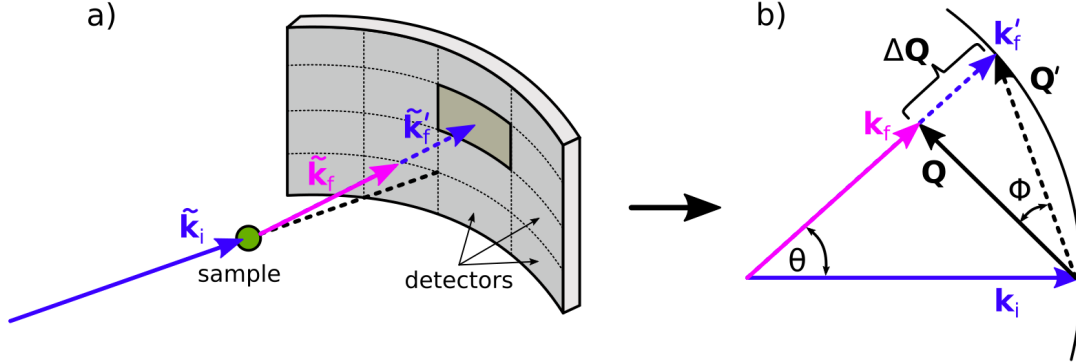
Fig. 2: a) Schematic of direct-geometry neutron scattering experiment. $\tilde{\boldsymbol{k}}_i$ is the incident neutron momentum in the lab frame. $\tilde{\boldsymbol{k}}_f$ and $\tilde{\boldsymbol{k}}'_f$ are the actual and effective final momenta in the lab frame. $\tilde{\boldsymbol{k}}_f \parallel \tilde{\boldsymbol{k}}'_f$ point to the same detector, but have different lengths: $\tilde{k}'_f = \tilde{k}_i = \sqrt{2E_i}$, while $\tilde{k}_f = \sqrt{2E_f}$. b) Scattering diagram in crystal coordinates. The actual change in momentum of a scattered neutron is $\boldsymbol{Q} = \boldsymbol{k}_f - \boldsymbol{k}_i$. The effective change in momentum assuming elastic scattering is $\boldsymbol{Q}' = \boldsymbol{k}'_f - \boldsymbol{k}_i$. The difference between the effective and actual scattering vector is $\Delta\boldsymbol{Q} = \boldsymbol{k}'_f - \boldsymbol{k}_f$.

dinates (time-of-flight, scattering-angle) to sample coordinates $(E, \boldsymbol{Q})$. Namely, we usually assume the all neutrons scatter elastically, $E = 0$. As explained below, this approximation introduces artefacts into the final data that may be misleading or misinterpreted.

2.1   Statement of the problem

In direct-geometry scattering, the change in direction and energy of a neutron is measured. Assume we know the incident energy, E_i, and incident direction, $\hat{\boldsymbol{k}}_i$, of the neutrons. Vectors with a "hat" are unit vectors, i.e. $|\hat{\boldsymbol{k}}_i| = 1$. From the neutron dispersion relation, $E_i = \hbar^2 k_i^2 / 2m \equiv k_i^2 / 2$, the incident momentum, $\hbar \boldsymbol{k}_i \equiv \boldsymbol{k}_i$ of the neutron is known (we use units with $\hbar = m = 1$):

$$k_i = \sqrt{2E_i}$$
$$\boldsymbol{k}_i = k_i \hat{\boldsymbol{k}}_i.$$

We can always determine the direction of the momentum of the final neutron by analyzing which detector it hits: the detector coordinates are known and can be converted to the sample coordinates. Call the direction of the scattered neutron's momentum $\hat{\boldsymbol{k}}_f$.

If we can measure the time-of-flight of the neutron and deduce the final speed, we can determine the final energy from $E_f = v_f^2 / 2$ and the final momentum from

$$\boldsymbol{k}_f = k_f \hat{\boldsymbol{k}}_f = \sqrt{2E_f} \hat{\boldsymbol{k}}_f.$$

The actual change in momentum and change in energy of the scattered neutron are $\boldsymbol{Q} = \boldsymbol{k}_f - \boldsymbol{k}_i$ and $E = E_f - E_i$ respectively (fig. 2). By conservation of energy and momentum,

these are directly related to the momentum and energy of the emitted/absorbed excitations in the crystal. E.g. if the neutron gains an amount of energy, E, the crystal must lose the same amount, $-E$. If the neutrons loses an amount of momentum, $-\boldsymbol{Q}$, the crystal must gain an amount, $\boldsymbol{Q}$.

If we can't determine the energy change, then we assume the scattering is elastic. We can still measure the direction of the final momentum, but we since we don't know the energy transfer, we assume the final magnitude is equal to incident magnitude: $k'_f = k_i$. The effective change in momentum, $\boldsymbol{Q}' = \boldsymbol{k}'_f - \boldsymbol{k}_i = k_i(\hat{\boldsymbol{k}}_f - \hat{\boldsymbol{k}}_i)$, is no longer exact.

In reality, this approximation can result in situations where we measure intensity at wave vectors $\boldsymbol{Q}'$ where there are no excitations in the crystal. Unless we are aware of these errors, we could misinterpret the TDS signal as interesting physics even in cases where the scattering is trivial.

2.2 Proposed correction

The easiest way to understand a TDS signal (or even elastic diffuse scattering or inelastic scattering) is by comparing to calculations. If we naively calculate TDS by calculating scattering cross sections, $I(\boldsymbol{Q}, E) = d^2\sigma/d\boldsymbol{Q}dE$, and simply summing over all energies at each $\boldsymbol{Q}$:

$$I(\boldsymbol{Q}) = \frac{d\sigma}{d\boldsymbol{Q}} = \int \frac{d^2\sigma}{d\boldsymbol{Q}dE} dE, \tag{1}$$

we will not account for the error discussed in the previous section. Comparing experimental TDS data containing artefacts of assuming elastic scattering for all neutrons to the calculation might lead us to misinterpret our experimental data.

We can't "reverse engineer" the experimental data without analyzing the energy of scattered neutrons. So the way around this is to correct the calculation to better represent the experiment; i.e. to include artefacts of assuming elastic scattering. Specifically, we pick a wave vector measured in the experiment, $\boldsymbol{Q}'$. Then, we determine what wave vectors, $\boldsymbol{Q}$, fall into the $\boldsymbol{Q}'$ bin if we impose $E = 0$ on all $(\boldsymbol{Q}, E)$ pairs.

The $(\boldsymbol{Q}, E) \to \boldsymbol{Q}'$ that map to a $\boldsymbol{Q}'$ bin depends on incident energy. For white beam, we discretize the incident beam into energies, $(E_i)_n$, and repeat this process for each incident energy in the beam.

The effective momentum transfer is (see fig. 2)

$$\boldsymbol{Q}' = \boldsymbol{k}'_f - \boldsymbol{k}_i = k_i(\hat{\boldsymbol{k}}_f - \hat{\boldsymbol{k}}_i). \tag{2}$$

$k_i = \sqrt{2E_i}$ is a known property of the incident beam. The actual momentum transfer is

$$\boldsymbol{Q} = \boldsymbol{k}_f - \boldsymbol{k}_i = k_f\hat{\boldsymbol{k}}_f - k_i\hat{\boldsymbol{k}}_i. \tag{3}$$

$k_f = \sqrt{2E_f}$ is fixed by the energy transfer, $E = E_f - E_i$. Define

$$\Delta\boldsymbol{Q} = \boldsymbol{Q}' - \boldsymbol{Q} = \boldsymbol{k}'_f - \boldsymbol{k}_f = (k_i - k_f)\hat{\boldsymbol{k}}_f = \Delta Q\hat{\boldsymbol{k}}_f. \tag{4}$$

with $k_i - k_f \equiv \Delta Q$. The squares of all of these vectors are

$$Q^2 = k_f^2 + k_i^2 - 2k_f k_i \cos\theta$$
$$Q'^2 = 2k_i^2 - 2k_i^2\cos\theta = 2k_i^2(1 - \cos\theta) \tag{5}$$
$$\Delta Q^2 = (k_i - k_f)^2 = k_i^2 + k_f^2 - 2k_i k_f = Q^2 + Q'^2 - 2QQ'\cos\phi.$$

See fig. 2. Note that $1 - \cos\theta = Q'^2/2k_i^2$ is fixed by the wave vector $\boldsymbol{Q}'$ and E_i we choose. Rearranging ΔQ^2, we find

$$(k_i + k_f)(1 - \cos\theta) = \cos\phi\sqrt{2(k_f^2 + k_i^2 - 2k_fk_i\cos\theta)(1 - \cos\theta)}. \tag{6}$$

Simplifying,

$$(k_i + k_f)\sqrt{1 - \cos\theta} = \cos\phi\sqrt{2[k_f^2 + k_i^2 - 2k_fk_i + 2k_fk_i(1 - \cos\theta)]} = $$
$$\cos\phi\sqrt{2[\Delta Q^2 + 2k_fk_i(1 - \cos\theta)]}. \tag{7}$$

Eliminating the $1 - \cos\theta$,

$$\frac{Q'}{2k_i}(k_i + k_f) = \cos\phi\sqrt{\Delta Q^2 + \frac{k_f}{k_i}Q'^2} \tag{8}$$

which can be rewritten as

$$\frac{1}{2k_i}(k_i + k_f) = \cos\phi\sqrt{\frac{\Delta Q^2}{Q'^2} + \frac{k_f}{k_i}}. \tag{9}$$

So finally,

$$\cos\phi = \frac{1}{2}\frac{(1 + k_f/k_i)}{\sqrt{(\Delta Q/Q')^2 + k_f/k_i}} \tag{10}$$

can be calculated from given quantities, k_i, k_f, ΔQ, and Q'.

2.3   What next?

This still doesn't fix $\boldsymbol{Q}$ uniquely since we don't know what plane $\boldsymbol{Q}$ and $\boldsymbol{Q}'$ span. It turns out that we need to know the scattering plane in the experiment to apply this correction. These data are available at the end of an experiment, but implementing this in an program will be a non-negligible amount of work. We leave this for the future.
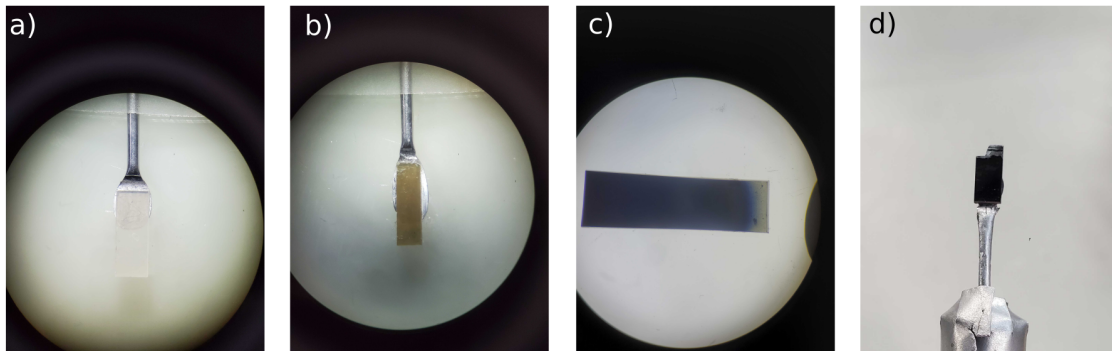
Fig. 3: Samples measured at CORELLI. a) Pristine $SrTiO_3$. Pristine TiO_2 and PMN-PT crystals look identical to a). b) PMN-PT flashed in vacuum. c) $SrTiO_3$ flashed in vacuum. d) TiO_2 flashed in vacuum.