Measuring Phonons in Crystals – Please Read Carefully!

Alfred Baron, 2010, 2016, 2022, 2023, 2025

The single most common point of failure of IXS experiments is insufficiently characterized or otherwise poorly prepared samples.

Any collaborator bringing a sample must insure it is the correct structure, single domain, of good quality, with known alignment and mounted appropriately on a holder compatible with BL instrumentation.

Below are some sample issue stories – these are real, and often involve experienced groups and good scientists who made incorrect assumptions, or did not check the work by their students or collaborators. If you have not done single crystal (4-circle) diffraction (with good results) on exactly the sample you intend to use for IXS, you can be setting up the IXS to fail. Note that Laue photos can be misleading for determining an azimuthal direction!

1. Sample was checked with Laue diffraction and appeared OK. Found in IXS to have large tails, poor mosaic -> poor data, impossible to get near to gamma.
2. Sample was checked using single crystal diffraction for only c-axis reflections. Found to be poorly ordered in ab plane while trying to set up for IXS -> IXS experiment impossible.
3. Sample had a complex structure that sample responsible thought they understood sufficiently but really did not -> wasted 2 days of IXS time trying to understand the sample.
4. Sample was too thin. Scans that should have been 2-3 hours needed 8-10 hours and even then the data quality was poor.
5. Sample had residual flux on it, leading to strange backgrounds in a low-rate experiment at small energy transfer -> experiment failed.
6. Sample was "known" to have a particular structure but, after the experiment was found to have a different (related) structure and not to be the intended sample. No publication.
7. Sample was a film expected to have a particular structure. While setting up for IXS it was found to be different than expected -> 3 days spent doing diffraction from the sample to understand it, 1 IXS spectrum only. After experiments sample determined to just be wrong. No publication.
8. Sample from INS people known to be twinned and expt. planned based on equal domain populations. But no twinning observed in IXS. Possibly better results, but expt. plan had to be changed on the fly.
9. Sample prepared by a student from an experienced group, but the PI did not check the Laue pattern. Cut so that the desired IXS experiments were not possible. -> lost ~1 day of IXS beamtime for re-cutting and polishing.
10. Sample looked pretty but not checked by diffraction. Extra phonon peaks observed indicating either significant impurity phase and/or multi-grain sample Data may be salvageable.
11. Sample mounted with known surface normal but azimuthal direction not checked – impossible to measure at optimal momentum transfers in the cryostat.
12. Sample measured with what was called single crystal diffraction but was not really (just a th-tth scan) – found to have at least two different domains.
13. Sample was flux grown. A small (broken off) piece checked by "single crystal diffraction" was found to be OK. In IXS alignment the orientation matrix could not be determined consistently from the surface of interest (Bragg geometry) for two samples. Another surface, however, was no problem. Explanation: one surface seemed to have multiple domains, others good. Note: clear difference in quality under microscope.
14. Laue the photo was apparently mis-read and the sample azimuth was 45 degrees from expected orientation. Also polishing caused a >10 degree difference of expected normal from real normal. BL staff had to spend most of a day aligning the sample (largest issue was PI expected the sample normal was good to couple degrees and it was not).

The following are some relevant points for measuring phonons in single crystals using IXS. Note, especially, that ***a sample prepared for neutron scattering, and especially for inelastic neutron scattering (INS), can sometimes be of poor quality for IXS measurements*** **(the constraints are just different for INS) – please be careful – see 7, below.**

0. Laue/Transmission vs. Bragg/Reflection Geometry. One sometimes, especially when cutting a crystal from a large piece, can choose to use either a transmission geometry or a reflection geometry (Laue and Bragg, respectively). Generally, if one knows the specific momentum transfer of interest, a reflection/Bragg geometry will give higher rates (e.g. x2). However, a transmission

geometry will usually be more flexible, allowing access to more of reciprocal space. Of course, for a transmission geometry, the sample needs to be thin enough (see 2). Conversely, for a Bragg geometry, the sample must be thick enough so that we do not see scattering from any supporting material (e.g. the copper of the sample holder) behind the sample. See also the "xray_..." commands in SIXCIRCLE.

1. Larger (up to a few mm) is almost always easier. We can and do measure ~10 micron samples. But count rate is always an issue, and aligning a small sample is often harder than aligning a larger one, and also, there can be beam shifts during scans, or sample shifts on cooling, etc. 1mm samples are much easier, with, probably, ~2x2mm^2 faces being close to ideal. If larger than ~5 mm (or thicker than 2 mm), consider cutting a smaller piece, or talk to a local contact, to make sure the sample will fit.

2. Know the attenuation length. You should know the absorption length of your sample**.** This sets the scale for the size and possible interference/shadowing from surface features/roughness. It also sets the length scale for a transmission (Laue geometry) measurement. For transmission measurements, the sample should be 1 to 1.5 absorption lengths thick along the x-ray beam – and not more than 2. You can use http://henke.lbl.gov/optical_constants/atten2.html to estimate the attenuation length – usual phonon setup operates at 23724 eV / Si (12 12 12) or 21747 eV/Si(11 11 11) or 17794 eV (Si (999) for high pressure). See also the "xray_..." commands in SIXCIRCLE.

3. Pre-aligned samples are required. Knowing the alignment of the sample (i.e.: two non-parallel reflections, or two axes of the unit cell, etc, *not* just one surface normal) at the level of a few (say ±5) degrees is crucial. While we will refine the alignment on the spectrometer, to go searching for Bragg reflections from scratch is a waste of beam time.

4. The sample must be a SINGLE DOMAIN. Be sure your sample is a single crystal without, say, some tiny domains with a different orientation (as can easily appear in flux-grown crystals). The beam size is ~50 microns, and often does not illuminate the full sample, so if present, micro-domains can appear unexpectedly and lead to strange results. You are urged to put your sample on a 4-circle diffractometer and scan over ALL of symmetry allowed reciprocal space to insure no micro-domains are present. Note: **TWINNING,** should be avoided as this can impact (severely!) careful measurements.

5. Mosaic. The mosaic requirements for IXS are relatively relaxed by x-ray standards, unless you need either very good Q resolution, or want to work very near a Bragg peak, etc. Typically, 0.1 degree mosaic is not a problem. We begin to worry above 0.5 degrees. Of course, smaller mosaic is usually better.

6. Azimuthal Orientation is Important. The azimuthal orientation of the sample (ie: rotation about the scattering vector) has nearly no impact on the momentum transfer measured *by the analyzer crystal in the center of the arm*. However, it has huge impact on the momentum transfers seen by the other analyzer crystals and so can be very important to make proper use of the analyzer array (esp. for transverse modes). See the discussion in section 4.6 of http://arxiv.org/abs/1504.01098

7. FOR NEUTRON SCATTERERS. Please note well that *relative to neutron scattering,* x-rays see only the surface of the sample (see 2 above). That surface should be flat and unstrained, and, ideally, lightly etched and/or carefully polished. Be careful: even if the sample was great for neutron scattering, the surface might be of very poor quality for x-ray scattering.