IN1-LAGRANGE - the new ILL instrument to explore vibration dynamics of complex materials

Alexandre Ivanov, Mónica Jiménez-Ruiz and Jiri Kulda
Institut Laue - Langevin, 71 avenue des Martyrs, 38000 Grenoble, France

aivanov@ill.fr

Abstract. We report on the first experimental results obtained with the recently commissioned IN1-Lagrange spectrometer, which has replaced the old IN1 Be-filter setup used for studies of lattice dynamics and molecular vibrations in an extended energy range, typically used for materials containing light chemical elements, in particular hydrogen. Unlike its predecessor, IN1-Lagrange uses, in addition to a cooled Be-filter, a large area crystal analyzer to collect the scattered neutrons and to define their final energy of 4.5 meV. Using the available set of double-focussing monochromators the incident neutron energy on IN1 can be scanned over the entire range of 4 – 600 meV provided by the ILL hot neutron source. Thanks to its large solid angle of 2.5 steradian and flexibly tuned energy resolution in the range of 1 - 5%, the IN1-Lagrange setup offers an unprecedented sensitivity permitting very rapid data acquisition and revealing fine spectral features in ‘standard’ samples as well as efficient measurements of hydrogen vibrations in samples containing equivalent masses of H₂ as low as 100 µg.

1. Introduction
Neutron scattering is an extremely powerful technique in the study of atomic and molecular vibrations. Its sensitivity to all types of atomic movements makes neutron spectroscopy the experimental method of choice when detailed knowledge of the vibration spectrum of a material is requested – on the level of phonon dispersion in single crystals or vibrational density of states (VDOS) in polycrystalline samples. In spite of the integral character of the VDOS, it represents an invaluable input for calculating thermodynamic properties and evaluating forces acting between atoms and molecules constituting condensed matter. It is particularly important in the studies of new and applications related materials typically available in polycrystalline form only.

A number of neutron spectrometers suitable for VDOS measurements are available at existing neutron sources, both pulsed and steady state. For the measurements of VDOS in a large range of energy transfer, typically indirect geometry time-of-flight (TOF) spectrometers (see, for instance, [1]) are exploited such as TOSCA [2] at ISIS (Oxford, UK), which has become a benchmark instrument in the matter, or NERA [3] in JINR (Dubna, Russia). Further development of the TOSCA-type set-up is represented by the spectrometer VISION [4] recently commissioned at SNS (Oak-Ridge, USA). Instruments of this type use Bragg reflection to select a scattered neutron energy close to the wavelength cut-off edge of a beryllium filter, used to suppress higher order harmonics. They provide...
suitable energy resolution, monotonous and slowly varied as a function of vibration frequency, in the whole range of measurements. The other examples of filter-based indirect geometry spectrometers dedicated to vibrational spectroscopy are the TOF spectrometer FDS [5] at LANSCE (Los-Alamos, USA) and the reactor-based FANS [6] at NIST (Gaithersburg, USA).

Direct geometry chopper spectrometers (see also in [1]) with a large solid angle for scattered neutrons can be used in the VDOS studies on polycrystals too as they may be advantageous in certain energy ranges, depending on the incident neutron wavelength. However, if a broad energy range is to be sampled with more than an order of magnitude difference between minimal and maximal measured frequencies in the spectrum, as it is typical for vibrational spectroscopy, direct geometry instruments would require recording spectra with several incident neutron energies in order to provide suitable resolution conditions in the full range with the need for subsequent normalization.

In the following we describe another type of indirect geometry spectrometer, which combines the advantages given by the continuous beam from a reactor neutron source and a large accepted solid angle for neutrons scattered by the sample. The new instrument with the secondary spectrometer named IN1-Lagrange is installed at the hot neutron source of the high flux ILL reactor [7]. It replaces the former filter-analyser spectrometer (IN1-BeFilter) which had a limited scattering angle and modest energy resolution. The new instrument fully benefits from the new large double-focussing multi-face crystal monochromator supplying monochromatic beam in the intermediate and high neutron energy ranges (mosaic Cu220 and Cu331 crystal faces) as well as in the lower energy range (elastically bent Si111 and Si311 reflections).

2. Instrument description
The IN1-LAGRANGE (LArge GRaphite ANalyser for Genuine Excitations) secondary spectrometer setup (Fig. 1) is based on the space focussing of neutrons scattered by the sample in a very large solid angle, which are all then recorded with a relatively small single counter (a He3 gas detector). That is, contrary to typical TOF instruments, the increased solid angle is not accompanied by an increase in the counting volume and the corresponding background.

The focussing reflecting surface of ~1 m² is built around the vertical sample-detector axis from pyrolytic graphite (PG) crystals set to reflect neutrons with the fixed average energy of 4.5 meV. Altogether there are 612 crystal holders mounted on the solid mechanical structure so that the individual flat crystals are set tangentially to the calculated ellipsoid of rotation. The crystal sizes, their mosaic spread and the height of the part covered by PG crystals are optimised in a way such that all three corresponding contributions to the energy resolution are equal. It is important that the requested energy resolution of the instrument is achieved with a relatively low grade of the pyrolytic graphite.

The appropriately shaped beryllium filter is installed immediately after the sample in order to remove higher-order harmonics in the analyser reflections. The filter transmission below the cut-off is enhanced by cooling it to the base temperature (20 K) of a powerful closed-cycle helium refrigerator.

The resulting accepted solid angle (~0.8π ≈ 2.5 Steradian) is among the highest apertures open for scattered neutrons in the most ambitious instrument projects at present. At the same time it is realised within the highly compact characteristic spectrometer volume, about 1 m³ for the analyser + filter pumped volumes).

The carefully designed screen of boron-containing absorber is installed on the sample-detector axis in order to suppress the intense elastic scattering from the sample. Further reduction of the instrument background, contaminated with the high neutron energy components, is achieved through massive polyethylene shielding built around the whole analyser.

The whole instrument can be considered as a variant of a classical three-axis spectrometer with a very large barrel-like fixed-energy analyser. The major difference is in the changed trajectory for scattered neutrons: if the incident monochromatic beam is kept in the horizontal plane, the scattered neutrons propagate in the directions out of this plane, all around the vertical axis sample-detector. Such arrangement appears to be more convenient for positioning and handling the sample environment equipment (sample cryostat etc.).
Note that there are no mutually moving parts within the secondary spectrometer which is positioned as a whole around the monochromator in order to record the inelastic scattering spectra changing step-by-step the incident energy similarly to a typical experiment on a three-axis spectrometer. The energy transfer (it is always, at IN1-Lagrange, a neutron energy loss in the scattering), which corresponds to excitation energy in the sample, is obtained by a subtraction of the analyser energy of 4.5 meV from the energy of incident monochromatic neutrons.

Figure 1. Left panel: the IN1-Lagrange analyzer scheme, two different vertical cuts; right panel: the IN1-Lagrange spectrometer assembled for the first tests with neutrons.

3. Results of the instrument commissioning
The first inelastic scattering spectrum measured with IN1-Lagrange is presented in Fig. 2. For characterisation of the instrument performance a sample of 2,5-diiodothiophene, \((\text{CH})_2(\text{Cl})_2\text{S}\), has been used. This material is known to exhibit very sharp vibration lines at low temperatures so that it can be used as a standard for measurements of the spectrometer resolution [8]. The visible sharp peaks in the energy spectrum in Fig. 2 are due to vibrations involving hydrogen atoms. These atoms are present in a relatively small quantity: the hydrogen partial weight in the measured sample amounts to 6 milligram. The collected statistics in the energy interval below 200 meV, left panel on the Fig.2, correspond to some 12-30 seconds measuring time per point, so that this informative energy interval could be scanned in less than 2 hours while the whole scan time for the shown spectrum, up to 600 meV (both panels of Fig. 2), is about 4 hours. The observed about an order of magnitude gain in the count rate on IN1-Lagrange with respect to the IN1 Be-filter setup is found to be in a very good agreement with the project predictions.
Figure 2. The inelastic scattering spectrum recorded with the IN1-Lagrange analyser. Note the different energy scales of the two panels. The sample of 2,5-diiodothiophene is cooled to the cryostat base temperature of 2.5 K. The measurement has been performed in a “fixed-monitor” regime with the 2D-focussing Cu220 monochromator reflection. The intensity is as-measured, without any further treatment, no background (cryostat and sample holder) has been subtracted. The energy resolution of IN1-Lagrange can be further improved in the broad energy range using the available Cu331 reflecting plane of the IN1 monochromator and introducing fine collimators in the monochromatic beam. As it is seen from the spectra presented in Fig. 3, many more fine details of the vibrational density of states are revealed in the higher resolution run with the Cu331 face at the expense of a solely ~2-fold decrease in the detector count rate. The change-over between different resolution settings can be done on IN1-Lagrange in less than half-an-hour thus offering very flexible conditions for optimising measurements with respect to the resolution vs intensity choice.

Figure 3. A fragment of the 2,5-diiodothiophene vibrational spectrum measured with different monochromator reflections, Cu220 and Cu331, and a 20’ slit collimator in the monochromatic beam. No background has been subtracted. Notice the change in the horizontal axis scale in the different energy ranges. The counting time per point, for the chosen monitor counts, was about 20-30% higher in the case of the Cu220 monochromator what corresponds, with the presented intensity scales, to about a factor of 2 intensity decrease, if normalized to the same counting time, for the high-resolution setup with the Cu331 reflection.
The measured line-widths with the sample of 2,5-diiodothiophene are presented as points in the Fig. 4 which also shows calculated energy resolution curves with different analyser and monochromator settings. Similarly to the predictions of the intensity gain, the resolution performance is in full agreement with what was expected from the pre-project estimations.

**Figure 4.** Calculated (lines) and measured (points) relative energy resolution of IN1-Lagrange with different primary spectrometer settings. No adjustable parameters are used in calculations which are based on the geometry of the incident and the scattered beam paths. The black line corresponds to the Be-Filter analyser resolution with the Cu220 monochromator, blue line – IN1-Lagrange with the Cu220 monochromator, red line – IN1-Lagrange with the Cu331 monochromator. These calculations are made for the natural collimation of the ‘in-pile’ beam tube of IN1 and 20’ Soller collimator in the monochromatic beam. Points are the peak widths divided by the peak energies as measured at the corresponding conditions with the 2,5-diiodothiophene sample. The scatter of points is most probably due to an uncertainty in the local background close to a line while fitting scattering intensity profiles to Gaussian line shapes. The lowest broken line represents the best-expected future energy resolution of the IN1-Lagrange. It is achieved with about 4-5 fold decrease in peak intensity as compared to the presented Cu331 data.

Further improvements in the resolution power of IN1-Lagrange are envisaged in the near future when the collimator changer will be installed before the monochromator, the work is awaiting the planned change of the reactor beam tube. The best energy resolution, achieved with 10’ slit collimators before and after the monochromator, will approach 1% in the energy range 100-200 meV as shown in Fig. 4. This ultimate energy resolution, positioning IN1-Lagrange at the top of high-resolution neutron spectrometers worldwide, will bring new motivation for progress in theoretical model and *ab-initio* calculations for existing and future functional materials.

The new possibilities offered by IN1-Lagrange in the low energy range are illustrated in Fig. 5 by measurements with the Si111 face of the monochromator. The two transitions between energy levels of Pr*+* ion split by the electric crystal field are clearly seen in the spectrum recorded with a resolution
of ~0.8 meV limited in this energy range mainly by the analyser. We estimate that with IN1-Lagrange useful information on the excitation spectra can be obtained starting from energy transfers as low as ~1.5 meV.

The luminosity power of IN1-Lagrange has been challenged with a small sample of 2,5-diiodothiophene. The energy spectrum of the sample containing only 100 microgram of hydrogen is presented in Fig. 6. All the principal vibration lines can be identified in spite of some noise present between the lines. Such “vanishingly small” quantities of scattering matter have so far been considered as impossible for neutron spectroscopy in this energy range. The excellent performance of IN1-Lagrange with small samples is confirmed in subsequent experiments (e.g. [9], and others).

**Figure 5.** The spectrum of low-energy crystal field excitations of Pr$^{3+}$ ions in a test sample taken at $T=4$ K with Si111 monochromator reflection. The horizontal axis represents the neutron energy loss in the scattering.

**Figure 6.** The spectrum of a 17 mg 2,5-diiodothiophene sample (containing 0.1 mg of hydrogen) obtained as a difference of the scattering intensities measured on IN1-Lagrange with the sample and with an empty sample can. Both runs in the shown energy transfer range took less than 8 hours each with the Cu220 2D-focussing monochromator.
We outline that with IN1-Lagrange, in contrast to the time-of-flight spectrometers, one can concentrate on a selected energy interval when detailed knowledge of the entire spectrum is not required. Thus the available beam time can be used for improving statistics in the most important spectral region of the measured VDOS or for detailed records of the effect of the sample environment conditions (variation of temperature, pressure etc.).

It is clear that the possibility of measuring good quality spectra from very small samples, including tempting studies at high pressures, will be strongly challenged by the instrument background. Our preliminary data are promising and we expect further progress in characterisation and reduction of this important component of the instrument performance for research with extremely small samples.

4. Conclusion

The new spectrometer IN1-Lagrange at the hot neutron source of the ILL high flux reactor has been successfully commissioned and is now in routine use for user experiments. The boost of sensitivity offered by IN1-Lagrange opens new possibilities in spectroscopic studies of modern functional materials. The new instrument permits investigation of much smaller sample quantities, inherent in novel materials studies, and a more detailed probing of external parameters like temperature, pressure, chemical composition, time-dependent processes etc. The improved energy resolution provides access to a higher level of detail in the vibrational spectra over the whole energy range, thus stimulating further development of theoretical models and \textit{ab-initio} calculations.

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