Cryogenic Raman Imaging for Low-dimensional Materials

An advanced microscopy system enables correlative measurements near absolute zero in high magnetic fields with full polarization control.

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Interest in Raman spectroscopy at room temperature, as well as at cryogenic temperatures, has been increasing across a range of scientific fields over the past two decades [1 – 3]. Initially, the primary driver of cryogenic applications was the carbon nanotubes and graphene community. As a response to the needs of these researchers, attocube systems AG and WITec GmbH – world leaders in their respective specialties of cryogenic scanning probe microscopy and Raman spectroscopic imaging – teamed up to develop a commercial solution for cryogenic Raman microscopy.

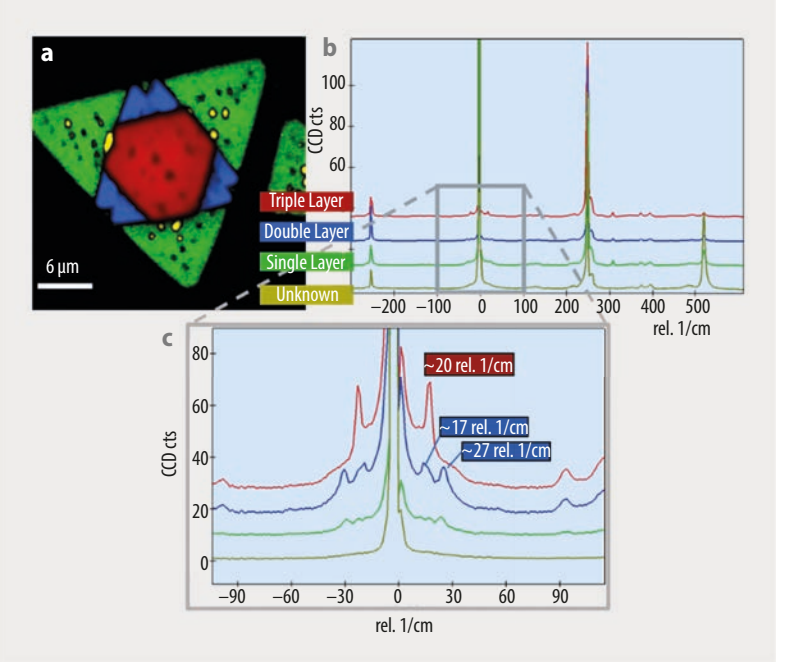

Fig. 1 Confocal Raman image of WSe_2 of various layer numbers at 120 K: combined false-color image showing the location of the different numbers of layers (a), Raman spectra of the layers in the corresponding colors (b) and zoom-in of the spectra around the Rayleigh peak (c).

Cryogenic Raman spectroscopy in high magnetic fields has become an indispensable tool for studying various novel materials. The technique is particularly useful for researchers focused on phase-transitions or emergent properties of low-dimensional materials with application potential in electronics or sensorics, such as transition metal dichalcogenides or van der Waals heterostructures. In order to meet these evolving market requirements, WITec and attocube developed cryoRaman, an advanced and modular cryogenic Raman microscope.

Building on previous co-development projects between the two companies and furthering the integration of the constituent technologies enables cryoRaman to deliver improved accessibility and configurability. Several new functionalities, such as low-wavenumber Raman peak detection, polarization control and the full automation of measurements, render cryoRaman tuneable to specific needs of different research fields. Moreover, with the combination of superior optics and the lowest-vibration cryostats, cryoRaman offers the highest data acquisition speed with unequalled lateral, depth and spectral resolution.

The outstanding performance of cryoRaman is only achievable by preserving the full capabilities of both companies' technology in combination. It is often difficult to achieve high confocality within a cryogenic system because the bore size of the magnet leaves little space and optical access is hindered. A proven solution to this problem is found in attocube's low-temperature objectives. The LT-APO objectives are designed for, and tested at, low temperatures and high magnetic fields. Unique in the marketplace, they offer outstanding optical performance, numerical apertures of 0.81 – 0.82, and their apochromatic ranges match all typical Raman laser wavelengths (532, 633, 785 nm) while enabling a lateral resolution of <400 nm in confocal scanning.

High resolution Raman map creation is facilitated by a direct elec-

tronic interface between WITec's scan controller and attocube's cryogenic piezo scanners. This makes it possible to program all typical Raman and photoluminescence measurements within WITec's Suite FIVE control software. With attocube's patented slip-stick drive piezo steppers, the sample can be brought into focus and the sample's region of interest can be accessed.

Other features that enhance the system's flexibility and convenience include automated alignment and calibration, automated laser output adjustment and motorized switching between different excitation lasers and white light microscopy. With these functionalities cryoRaman has achieved a level of user-friendliness that makes high resolution confocal Raman imaging at cryogenic temperatures in high magnetic fields accessible to researchers of all experience levels.

The following measurements demonstrate cryoRaman's performance in investigations of two types of low-dimensional materials.

High resolution, low temperature confocal Raman imaging

A tungsten diselenide (WSe_2) flake on Si/SiO_2 was recorded at 120 K. The image is 30×30 µm² in size with 400×400 pixels (spectra) resolution and an integration time of 150 ms per spectrum. A 532 nm laser was used for excitation and the RayShield coupler allowed detection of Raman bands down to ~±10 rel. 1/cm. A UHTS300 spectrometer optimized for detection in the visible range with an 1800 g/mm grating and a back-illuminated CCD camera was used.

Inside the cryostat an attocube LT-APO 532-RAMAN objective with a numerical aperture of 0.82 and attocube piezoelectric positioners controlled through WITec's Control FIVE software were used. The acquired data set was evaluated with the Project Plus software package using the cosmic ray removal tool as well as background subtraction before TrueComponent Analysis was employed to automatically identify the sample components (**Fig. 1b**) by layer number. The images showing the WSe_2 in different numbers of layers were then combined in the false-color image (**Fig. 1a**). **Fig. 1c** shows a zoom-in of the low-wavenumber area with the most prominent peaks for the double and triple layers as labelled. The presence of the single, double and triple layers could be clearly identified by the peaks present. The unknown phase shows some of the characteristics of the single layer, but with an enhanced intensity of the Si-peak near 520 rel. 1/cm.

Temperature dependent photoluminescence

In an example of temperature-dependent measurements, part of the same WSe_2 flake was measured at varying temperatures. For this experiment, the photoluminescence signal was recorded instead of the Raman signal. The same hardware as described above was used, but the 600 g/mm grating was rotated under software control to a slightly different angle for this purpose.

The wavelength of the PL peak of the WSe_2 flake is recorded at different temperatures (**Fig. 2a–d**), and example spectra are recorded from the center and the edge of the flake for each temperature (**Fig. 2e**). The two- and three-layer areas of the flake did not emit significant signals, as was expected. It can be seen that the PL peak near the edge is shifted to lower wavelengths (higher energies) at all temperatures. Such a shift in the photoluminescence peaks of WSe_2 flakes has already been reported for room temperature experiments [4]. Additionally the peak shift as well as the peak sharpening with decreasing temperature is illustrated (**Fig. 2e**).

Magnetic field- and polarization-dependence

In order to demonstrate the dependence of Raman signals on polarization in varying magnetic fields, experiments were performed following the examples shown by Yang et al. [5] and Ji et al. [6]. For this a molybdenum disulfide (MoS_2) flake on Si was imaged at < 2 K while both the magnetic field as well as the polarization was varied. The location chosen on the sample contained a flake consisting of different numbers of layers.

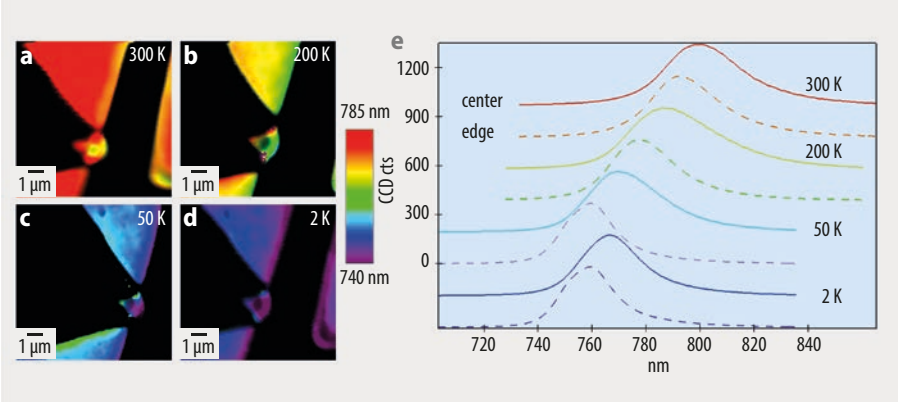

Fig. 2 Confocal photoluminescence imaging scans of WSe_2 at varying temperatures: peak position images at varied temperatures (a–d), normalized spectra (e) at each recorded temperature with the solid lines representing the spectra in the center of the single layers and the dashed lines the spectra at the outer edge of the single layers, respectively.

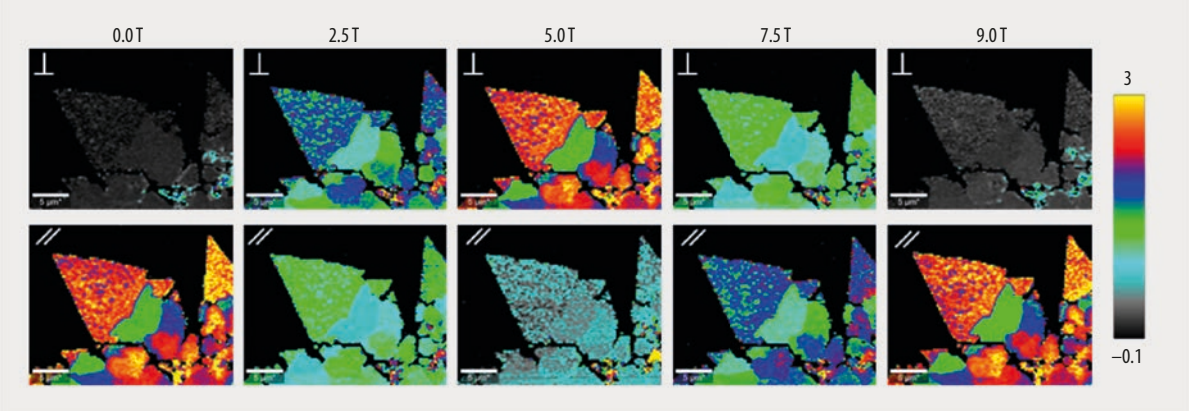

Fig. 3 Cryogenic Raman images of MoS_2 under different conditions. The A'_1 / E'-intensity ratio recorded at 2 K for different magnetic field strengths and polarization states: perpendicular orientation of polarizer and analyzer (top), parallel orientation (bottom).

The optimal parallel configuration for the polarizer and analyzer was determined by iteratively rotating the polarizer and analyzer until the A'_1 Raman signal of a single layer of MoS_2 was maximized. For the measurement in the perpendicular configuration the analyzer was then rotated by 90°.

The flake was imaged using 532 nm excitation (8 mW before the objective) through a RayLine filter set and a UHTS300 spectrometer with a 1800 g/mm grating and a back-illuminated CCD camera. The objective was again a LT-APO 532-RAMAN objective with a numerical aperture of 0.82. Images were recorded with an image size of 28×22 µm^2 with 112×88 points per image and an integration time of 0.15 s per spectrum. Images using identical parameters were recorded in varying magnetic fields and in parallel and perpendicular polarization configurations, respectively. The integrated intensity of the A'_1 Raman signal of MoS_2 was normalized against the integrated intensity of the E' peak for each measurement and all images in **Fig. 3** are coded using the same color scale. Pixels at which no E' peak was present were suppressed in the visualization below to enhance clarity and the lower limit of the color scale was intentionally set to –0.1 in order to visualize the flake even in configurations where no A'_1 Raman signal was detectable (dark gray areas).

The change in suppression of the A'_1 Raman signal from perpendicular to parallel polarization configurations as the magnetic field is increased from 0 to 5 T, and back again when approaching 9 T, is in good agreement with [5]. However, in [6] this change could only be detected at significantly higher magnetic fields. Yang et al. [5] propose the low temperature used in their experiments as a potential explanation, which was also the case in our experiments.

While influence of the perpendicular magnetic field on the oscillation modes of the crystal seems plausible, it is important to consider the impact of the Faraday effect. It causes a rotation of the polarization axis when light travels through transparent media in the presence of a magnetic field. In practical terms this means that the polarization axis of the light is rotated after passing through the LT-APO objective by an angle that correlates linearly with the magnetic field strength. Using the motorized polarization control this could, however, be automatically compensated for after characterization of the objective.

Conclusion

As demonstrated conclusively in the measurements above, cryoRaman offers a wide range of experimental possibilities. In the attoDRY2100 cryostat the sample base temperature is <1.8 K and is variable up to 300 K. Within this temperature range, Raman and photoluminescence peaks can be observed, and their temperature-dependent shifts and changes are of great interest in the study of phase transitions. Raman peaks down to 10 rel. 1/cm are conveniently detected and polarization control offers many possibilities in the field of spin-valley physics. This is complemented with unidirectional and vector magnet options.

Altogether, cryoRaman's unique capabilities provide a powerful new tool for low-dimensional materials characterization at cryogenic temperatures.

[1] *T. P. Devereaux* and *R. Hackl*, Rev. Mod. Phys. **79**, 175 (2007)
[2] *C. S. S. R. Kumar* (Ed.), Raman Spectroscopy for Nanomaterials Characterization, Springer (2012)
[3] *M. Paillet* et al., J. Raman Spectrosc. **49**, 8 (2018)
[4] *U. Schmidt* et al., Spectroscopy **36**, 23 (2021)
[5] *Y. Yang* et al., J. Phys. Chem. C **124**, 17418 (2020)
[6] *J. Ji* et al., PNAS **113**, 2349 (2016)

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