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Electron energy loss spectroscopy of excitons in two-dimensional-semiconductors as a function of temperature

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We have explored the benefits of performing monochromated Electron Energy Loss Spectroscopy (EELS) in samples at cryogenic temperatures. As an example, we have observed the excitonic absorption peaks in single layer Transition Metal Dichalcogenides. These peaks appear separated by small energies due to spin orbit coupling. We have been able to distinguish the split for MoS₂ below 300 K and for MoSe₂ below 220 K. However, the distinction between peaks is only clear at 150 K. We have measured the change in absorption threshold between 150 K and 770 K for MoS₂ and MoSe₂. We discuss the effect of carbon and ice contamination in EELS spectra. The increased spectral resolution available made possible with modern monochromators in electron microscopes will require the development of stable sample holders which reaches temperatures far below that of liquid nitrogen. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4947058>]

The physical properties of materials can change drastically as their size reduces. Typically, this occurs when a characteristic length scale, intrinsic to the material, is crossed. For the optical properties of semiconductors this scale is given by the exciton Bohr radius. Although this quantity may vary greatly, for many technologically important materials it is in the nanometer range (GaAs 12.4 nm,¹ GaN 2.8 nm,² MoS₂ 7 nm from calculations³). For sizes around and below this value confinement leads to the appearance of discrete energy levels and drastic changes in the absorption and emission spectra.¹ As this effect is intrinsically linked to small objects, techniques able to access optical information at the nanometer scale are fundamental. Electron energy loss spectroscopy (EELS) in a transmission electron microscope (TEM)⁴ allows measurements of optical properties far below the diffraction limit.^{5,6} Recently, we have discussed the benefits of using EELS to measure excitons in two-dimensional Transition Metal Dichalcogenides (TMD).⁷ The energy resolution in EELS experiments can be of the order of 1 meV,⁸ allowing vibrational spectroscopy using electrons as the excitation source. However, experiments with such energy resolution are performed in setups with low spatial resolution. Up until recently, EELS in a TEM was typically limited to about 100 meV.^{9–11} Recent results have shown that EELS at much higher spectral resolution (at or below 20 meV) and at high spatial resolution is possible.^{7,12–14}

In this letter, we discuss the influence of sample temperature for excitons absorption measurements in TMD using EELS. We show that for MoSe₂, the two exciton peaks separated by 220 meV are only distinguishable below 220 K and clearly visible at 150 K (for the same experimental conditions). A similar behavior is observed for MoS₂.

The crystal structure of these materials (space group $P6_3/mmc$,^{15–17} with a hexagonal symmetry) is composed of a basic unit of three layers: a layer of a transition metal between and covalently bonded to two layers of a chalcogenide. The interaction between two of these basic units is through van der Waals force,¹⁵ leading to a crystal which is easily cleaved into monolayers.¹⁸ Bulk crystals of MoS₂ and MoSe₂ show an indirect band gap with the valence band maximum at the Γ point and the conduction band minimum between the Γ and K points.^{17,19} However, for monolayers, a direct band gap in the K point is observed,^{18,20–22} which occurs due to a relative increase in energy of the maximum in the K point with respect to the one at the Γ point.²³ For the monolayers, the hole mass increases, leading to poorer hole mobility.²³ The existence of this direct gap at the K point has been inferred^{24,25} before recent experiment showing large photoluminescence increase for monolayers.^{18,26}

EELS experiments have been performed on a double corrected JEOL ARM equipped with a Schottky field emission gun, a JEOL double Wien filter monochromator, and an EEL spectrometer. A Gatan Quantum spectrometer, modified for low primary energy operation (15–60 keV), with improved electronics for higher stability was used. EELS experiments have been performed in scanning mode using 60 keV electrons (experiments were also performed at 30 keV with no significant spectral difference observed). Minor damage was observed in both samples at the experimental condition used. After a whole set of data acquisition, no detectable spectral change was observed. Typical parameters of the probe were as follows: energy profile FWHM between 20 and 50 meV; convergence semi-angle of 47.7 mrad. The EELS collection semi-angle was about 100 mrad. Even though we integrate a large angular range, most of inelastic scattering is peak at small angles.^{4,27} In any case, using a convergent probe, different scattering angles will be always mixed to some extent.

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The energy dispersion of the spectrometer was set between 2 and 5 meV/channel. Experiments at or below 300 K were performed with a Gatan liquid nitrogen sample holder (Gatan, Model 626DH J5 UPR). Experiments above 300 K were performed with a JEOL heating holder (JEOL, Model EM 21130). EELS maps have been acquired using the dual-EELS mode, where a fast acquisition (1 ms time scale) in series with a long acquisition (100 ms to 1 s time scales) allows the observation of the unsaturated zero-loss peak and the desired spectrum. The long acquisition times used for the higher-loss spectra did not lead to a substantial energy resolution loss. The dispersion of the spectrometer was checked over long time scales showing no significant changes. The experimental configuration allows concomitant acquisition of atomically resolved High Angular Annular Dark Field images (HAADF, Figs. 1(a) and 1(b)) and high spectral resolution EELS data (Figs. 1(c) and 1(d)). EELS measurements were realized at the same region of each sample, with repositioning of the electron beam between measurements using HAADF images. For each set of measurements, the same region of a monolayer was used to avoid effects of bending and strain in the data. Experiments on MoSe₂ were performed on MoS₂(1-x)Se_{2x} single layers. Regions of pure MoSe₂ within our experimental resolution were used. Single layer MoS₂Se₂(1-x) alloy was synthesized by two step CVD process. The as-grown single

crystal of MoSe₂ monolayer on sapphire substrate was sulfurized in a hot-wall furnace at 970 K to form single layer MoS₂xSe₂(1-x) alloy.²⁸ The MoS₂ experiments were performed in monolayers which suffered the complementary process (selenization of MoS₂ monolayers). These layers were transferred to TEM microgrid using clean transfer technique.^{29,30} Simultaneously, obtained HAADF images confirm that no contaminants/impurities are found in the analyzed regions.

The intensity in an EELS spectrum is proportional to the imaginary part of the dielectric function, $Im\{-1/\epsilon(\omega)\}$ for a bulk specimen. In principle, access to this quantity allows one to retrieve $\epsilon(\omega)$ using a Kramers–Kronig transformation.⁴ However, for a thin specimen, as required for STEM-EELS experiments, surface effects play an important role, complicating a direct and simple interpretation of low loss EELS spectra (even without considering more technical problems, as background subtraction). For thicker objects, other effects may play a role, as Cherenkov losses^{4,31} and the appearance of guided modes within the energy gap.^{4,32} Fortunately, for a two dimensional material (where TMDs, grapheme, or h-BN are the best approximation), its EELS spectrum is directly proportional to the imaginary part of $\epsilon(\omega)$, $\epsilon_2(\omega)$.³³ For this reason, one may more easily interpret the low loss EELS spectra of these materials.

In Figs. 1(a) and 1(b), EELS spectra of MoSe₂ and MoS₂ as a function of temperature between 150 K and 770 K are shown. In the spectra at 150 K (the one with the most information), two peaks (marked A and B) can be distinguished. These peaks are associated with two exciton states which are split due to spin–orbit coupling in both materials. The same effect has been observed in TMDs³ using light absorption techniques and in MoS₂ in EELS experiments.^{7,34} The position of the A exciton and the spin–orbit splitting were 1.69 eV (1.99 eV) and 220 meV (150 meV) for MoSe₂ (MoS₂). These values for MoSe₂ are slightly larger than the ones previously reported by us in an earlier report⁷ (1.64 eV and 190 meV), but they are within the energy resolution of these experiments. The value for the MoS₂ A exciton is 100 meV higher than our previous report (although the splitting is the same). The A and B excitons are also visible at 300 K for MoS₂. At this temperature, the A exciton energy is 1.99 eV and the splitting is 120 meV. Possible sources of error are differences in temperature between experiments, errors in the absolute calibration of the spectrometer, and sample differences. For example, different levels of strain may shift the absorption peak position,³⁵ a quantity we did not track during our current experiments.

As can be seen in Fig. 1, for increasingly higher temperatures, the spectral features shift to lower energies and become broader. Even at 220 K, the A and B excitons can be hardly discerned for MoSe₂, even if the spectral resolution (FWHM of the zero-loss peak) was the same within 10 meV. These features can be observed up to 300 K for MoS₂. For this reason, the exciton peaks cannot be used as a measurement of the spectral changes. A quantity that can be used is the threshold energy, which is measured by fitting a linear function to the first rise of the EELS spectrum and extrapolating its value to zero intensity (exemplified by the blue dashed line for 770 K on Fig. 1(b)). Still, this quantity is

FIG. 1. (a) and (b) Absorption spectra for MoSe₂ and MoS₂ as a function of temperature, respectively. For both materials, a shift to lower energy is observed for the absorption threshold, which was measured by fitting a linear function to the first rise of the EEL spectrum. A light blue curve exemplifies this process in (b). The splitting in the exciton peaks is observed at 150 K for both materials. Finally, a change in slope is seen for MoS₂ between 150 K and 300 K, which was observed in experiments at different dates. The insets show examples of HAADF image of MoS₂ (770 K) and MoSe₂ (150 K) acquired with the conditions used for the EELS experiments.

prone to uncertainties, mainly due to how the zero-loss peak is subtracted from the data. Zero-loss subtraction was necessary, as the high energy tail of the zero loss peak is still present at around 1.5 eV. Another possible source of uncertainty is absorption due to Cherenkov radiation. However, considering the dielectric constant of MoSe₂, this Cherenkov radiation can be discarded for 60 keV electrons.^{4,31}

The value for the absorption threshold as a function of temperature for MoSe₂ is shown in Fig. 2, varying between 1.58 eV (at 150 K) and 1.26 (at 770 K). For MoS₂, this value varies between 1.82 eV (at 150 K) and 1.59 eV (at 770 K). The uncertainty in these values stems mainly from the FWHM of the zero-loss peak and its subtraction. The derivatives for the threshold as a function of temperature (150 to 770 K range) are -0.5 meV/K for both materials, which have been measured by a linear fit to the data. The variation of the threshold with temperature occurs due to changes in the atomic spacing in the material. We have observed that this quantity changes between different experimental datasets, within the estimated errors in the threshold values.

The energy shifts observed are qualitatively coherent with the observed changes in photoluminescence peak energy as a function of energy³⁶ and with calculations for the *K* point direct band gap for bilayer MoS₂.³⁵ Changes in electronic structure are related, in a first approximation, to changes in the crystal structure due to lattice expansion or contraction. However, this is not equivalent to applying strain to the layer. First of all, there is no simple connection between temperature and lattice changes in a large temperature range for all materials. Second, changes in the lattice by temperature cannot be easily mimicked by applying strain, given that such variations may be in all directions and anisotropic. Finally, close to the Fermi level, the electronic population is distributed according to a Fermi–Dirac distribution, with an energy width given by kT (k is the Boltzmann constant and T is the temperature in Kelvin), an effect which cannot be mimicked by strain. In our experimental range, this quantity changes between 13 meV and 64 meV.

Returning to the energy thresholds, for MoS₂, the spectrum at 150 K seems to have a different slope close to the threshold when compared to the higher temperature spectra. This behavior has been observed in different experiments. However, we have no clear explanation to this observation.

FIG. 2. Absorption spectra energy threshold as a function of temperature for MoS₂ and MoSe₂.

One possibility is the presence of carbon contaminants at 150 K experiments (which were not observed in the MoSe₂ experiments). At room temperature and at 150 K, a dip at 2.30 eV (which is also reproducible between different samples and datasets) has been observed for MoS₂. Further investigation is necessary to fully understand these effects.

Therefore, understanding the effect of contamination in the spectra is important. In Fig. 3, we have shown examples of a clean MoS₂ spectrum at 300 K (red) compared to the one acquired at 300 K with carbon contamination (black) and at 100 K with ice contamination (blue). Spectral information is clearly lost, due to a mixture of the absorption signature of different materials. At 100 K, the two peaks which should be observed are seen as a single large peak due to the ice contamination. Therefore, the presence of contaminants is very detrimental to the observations of fine spectral structures. For this reason, spectra must be acquired with very clean samples.

The benefits of using samples at cryogenic temperatures have already been appreciated in different electron microscopy techniques, such as higher stability under electron irradiation for imaging,^{4,27,37} electron diffraction,³⁸ and cathodoluminescence.^{39–41} Also, high energy resolution EELS (HR-EELS) on surfaces has already been performed at cryogenic temperatures for decades, mainly due to the increase of the FWHM of absorption peaks as a function of temperature. With our results, we return to this idea, showing that current developments towards 1 meV EELS resolution in a TEM will induce the need for experiments with samples at cryogenic temperatures using dedicated sample holders, able to cool down samples to liquid helium temperatures. With the fact that experiments will be performed with lower beam currents (due to monochromation) and at higher dispersions (due to increased spectral resolution), new holders will require mechanical stability compatible with precise positioning of an Ångström-wide electron beam for long exposures.

Moreover, although the physics of excitons has been explored for decades and that of 2D materials is the subject of intense research, there is much to be learned about these excitations by linking spatial and spectral (possibly, multiple spectroscopies such as EELS and cathodoluminescence) information of individual structures (in parallel with the state-of-the-art calculations), stressing the need for the below liquid nitrogen temperature stable holders for TEM.

FIG. 3. EELS spectra of MoS₂ showing the effect of carbon contamination: clean sample at 300 K (red), carbon contamination at 300 K (black), and ice contamination at 100 K (blue).

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