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Thermal properties of 2D materials in the monolayer limit: Raman scattering techniques

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Raman spectroscopy has become the most suitable method to measure the thermal conductivity of two dimensional (2D) semiconductors (also named layered or van der Waals materials) in a few layer samples or in the monolayer (ML) limit. Raman spectroscopy is an optical technique, therefore avoids the use of contacts, which can complicate the modelization of the experiment, masking the real values of the thermal conductivity of the 2D material. The technique employs a laser as the heating element and the Raman signal as a thermometer. In its simple set up we need a laser, which can be focused on the flake of the material with a high magnification objective and a single monochromator with an edge filter can be used to monitor the temperature. The in-plane thermal conductivity is obtained by appropriately modeling the experiment. Care has to be taken in designing the experiment to simplify the theoretical model and control all possible sources of errors and uncertainties. In this work, we discuss the fundamental principles of the method, the details of the theoretical modeling, the approximations made in the model and the main uncertainties giving rise to over- or under estimations of the thermal conductivity. We also advise from wrong interpretations found in the literature. Finally, a list of thermal conductivity values of 2D materials is given and discussed. © Anita Publications. All rights reserved.

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1 Introduction

In 2003, the Russian physicists Andre Geim and Kostantin Novoselov were able to exfoliate graphite until they obtained graphene, a one layer graphite, it is thus the thinnest material ever known [1]. Graphene has applications in many fields, probably the most interesting one in materials science being in energy [2]. With the graphene revolution, other layered materials, mainly semiconductors, but also superconductors or even two dimensional metal nanostructures, have attracted the interest of physicist and chemists [3]. The so called two dimensional (2D) materials are however not strictly 2D as graphene, they consist of two or a few atomic layers, even that emulating graphene (silicene, germanene, phosphorene, antimonene) [2,4,5]. The interest in 2D materials is focused in a few layers or in the monolayer limit, in the exploration of nanodevices combining properties (photonics, phononics, magnonics and topology) at the nanoscale. But, what is a monolayer (ML)? The transition metal dichalcogenides MX₂ (TMDC) consist of one metal atom (Cr, Mo, W) surrounded by two chalcogen atoms (S, Se, Te) forming three-layer cakes, separated each other by van der Waals forces, thus a monolayer consists of three layers. The family of M₂X₃ (Bi₂Se₃, Bi₂Te₃, Sb₂Se₃, Sb₂Te₃) for instance, have a quintuple layer structure. Most of these materials are, into the bargain, topological insulators [6,7]. The applications of 2D materials are in the field of optoelectronics/ nanoelectronics, spintronics, thermoelectricity, energy storage (supercapacitors), gas sensors, and so on [8].

The interest in 2D materials can be brought to light by looking at the number of entries in the web of sciences: close to 200 thousand entries. There is a growing interest in 2D materials, not only due to the envisioned applications, but also to the new physical properties arisen related to topology or magnetism.

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They are formed by a stack of layers ordered in the space in different ways and thus crystallizing in different space groups, there are simple hexagonal materials like the well known $MoSe_2$ or triclinic materials like ReS_2 . The GaX (X=S, Se, Te) material for instance has a hexagonal packing in the case of GaS and GaSe, but GaTe is monoclinic since the size of Te does not allow the accomodation in a simple packing. Also, InSe or GaSe crystallizes in different polytypes, depending on the growth conditions. In any case, in the ML limit most of the materials are hexagonal. In many of the applications of 2D materials the thermal conductivity is a key parameter. But the thermal conductivity of a few layers materials is also of fundamental interest. Does the thermal conductivity changes with the number of layers? If the answer is yes, why? This point will be commented later when discussing the experimental results of different materials.

Raman spectroscopy is an optical method especially suitable for examining molecular vibrational modes or phonons in solids. This technique involves the analysis of inelastically scattered light from a monochromatic laser beam interacting with a material. The heat can be carried out by electrons and phonons, but in non conducting materials the heat transport is mainly due to phonons, making Raman spectroscopy a suitable tool to study the thermal conductivity in 2D materials. Actually, Raman spectroscopy is one of the few methods able to measure the thermal conductivity up to the monolayer limit. Raman peaks shift with temperature due to anharmonicity and thermal expansion. Using Raman thermometry, it is possible to map the temperature along a device [9,10] but also look for highly efficient materials to improve heat dissipation in power electronics [11]. In the last few years, Raman has become a common method to determine the thermal conductivity in 2D materials in the monolayer limit [12-22]. Typically, a flake of 2D material is transferred onto a substrate that has been pre-patterned with micro-holes of radius *R* and coated with a metal layer to establish effective thermal contact, the laser is positioned at the center of the hole (see Fig 1) to have cylindrical symmetry and emulate the experimental conditions by using an appropriate heat diffusion model.



Fig 1. Left: A perspective of the substrate with holes, coated with Au, the flake on top of a hole and the laser focused on the sample through a microscope objective is shown. Right: A lateral view of a sample consisting of 1 ML is shown on top of the Au-coated substrate. The laser spot is focused on the centre of the sample. The curve in red accounts for the heat distribution; in the suspended region heat dissipates laterally (shadowed in red), while in the supported region the heat dissipates through the Au-coating.

In the next sections, we will describe the theoretical model, will pay attention to the different sources of uncertainties, recommend the essential elements for a solid setup, and discuss the results obtained in a large list of 2D materials. Finally, we will summarize the main conclusions of the work.

2 Thermal conductivity

The heat conduction is governed by the so called Fourier's law, which states that the heat flow density q (W/m²) is proportional to the temperature gradient,

$$q = -\kappa \nabla T, \tag{1}$$

 κ (W m⁻¹K⁻¹) being the proportionality constant and the minus sign indicates that the heat flows from the hot side to the cold side of a body. The thermal conductivity κ is actually a second-rank tensor which can be diagonalized, obtaining three principal values κ_1 , κ_2 and κ_3 , that means that the heat flow, in general, does not follow the direction of the temperature gradient, it depends on the anisotropy of the material. In 2D materials, in most of the cases, we have two components, the cross-plane conductivity κ_{\perp} (perpendicular to the layers) and the in-plane conductivity κ_{\parallel} (parallel to the layers). Moreover, the thermal conductivity is temperature dependent. In MoS₂ for instance, the in-plane thermal conductivity reduces a 10% when the temperature increases from 200 to 300 K [23], obviously due to the increase of the phonon population. Since it is clear that the methods based on Raman scattering measure the in-plane thermal conductivity, we will drag the subindex (κ_{\parallel}), unless we need it to distinguish from other methods. We will include the distinction whenever needed.

The heat equation corresponding either to an isotropic medium or particularizing for the in-plane thermal conductivity reads

$$\kappa \nabla^2 T + S = C \frac{\partial T}{\partial t} \tag{2}$$

where $S(W/m^3)$ is the volumetric heat generation and $C(JK^{-1}m^{-3})$ the volumetric heat capacity (in a solid, $C_p = C_v \equiv C$). $\kappa/C = \alpha$, the thermal diffusivity (m²/s). α decreases with temperature as κ decreases.

2.1 Simplified problem: Solution for a hollow cylinder

Let us solve first the problem of a hollow cylinder of internal radius r_0 and external radius R with thickness d. We assume that the heat source is just at the inner cylinder wall. The heat flow rate Q(r) (W) dissipates radially as shown in Fig 2. If there are no losses, the heat flow rate will be constant at any distance from the center of the cylinder, thus the heat flux times the lateral surface area, $q_r 2\pi r d$, will be constant, therefore

$$r\frac{\partial I}{\partial r} = C_1$$

$$T_2$$

Fig 2. Heat diffusion in a hollow cylinder.

Integrating the equation,

$$T(r) = C_1 \ln r + C_2$$
 (4)

The integration constants can be found from two boundary conditions. Choosing $T(r_0) = T_1$ and $T(R) = T_2$, we have

$$T = T_1 + (T_2 - T_1) \frac{\ln(r/r_0)}{\ln(R/r_0)}$$
(5)

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which can be written as

$$\frac{(T_1 - T)}{(T_1 - T_2)} = \frac{\ln(r/r_0)}{\ln(R/r_0)}$$
(6)

From the T(r) dependence, we can calculate the flow rate

$$Q = 2\pi d\kappa \frac{T_1 - T_2}{\ln(R/r_0)} \tag{7}$$

Let us try to write the above equation in terms of the thermal conductance (G_{th}) or the thermal resistance $(R_{th} = 1/G_{th})$. In a wire of length *l* and surface *S*, the thermal conductance can be written as $G_{th} = \kappa \times S/l$, in the same way as the electrical conductance $G = \sigma \times S/l$ (or the electrical resistance $R = \rho \times S/l$, ρ being the electrical resistivity; $\rho = 1/\sigma$). The thermal conductance is given in W/K while the thermal resistance (R_{th}) has units of K/W. From Eq (7), the thermal resistance can be written as

$$R_{th} = \frac{\ln\left(R/r_0\right)}{2\pi d\kappa} \tag{8}$$

But, what is the meaning of the thermal resistance? Looking at Eq (8), if the thermal conductivity is infinity, when we heat the cylinder at r_0 , the heat will arrive at R instantaneously. If the thermal conductivity is zero, the heat never arrives at R. Thus, the thermal resistance represents the difficulty of the heat to be transferred from r_0 to R. Thinking of phonon transport, at low temperatures the phonon population is very small, thus, the thermal conductivity must be small, while at high temperatures the phonon population is high and the thermal conductivity must increase. If the phonon transport is hindered due to nanostructuration, the thermal conductivity decreases and the thermal resistance increases. Thus, the purpose of nanostructuration is to increase the thermal resistance or, equivalently, decrease the thermal conductivity.

Therefore, from Eq (8), we can deduce the thermal conductivity (κ) of the material from the knowledge of the thermal resistance as follows

$$\kappa = \frac{\ln(R/r_0)}{2\pi dR_{th}} = \frac{\ln(R/r_0)}{2\pi d} G_{th}$$
(9)

The thermal resistance (conductance) is an intrinsic property of the material, like the electrical resistance. But the thermal resistance (R_{th}) is different with thermal boundary resistance. The thermal boundary resistance is the loss of heat flow when crossing the interface between two materials (if the thermal boundary resistance is infinity, there is no heat flow crossing the interface).

2.2 Real problem: solution for a Gaussian distribution of heat

The problem to be analysed consists of a sample flake heated by a laser with a Gaussian profile. We have to pose mathematically the radial heat dissipation from the laser spot along the suspended and supported regions. In our experimental setup, we have a material flake of thickness *d* on a substrate where we have drilled holes of radius $R >> r_0$, r_0 being the radius of the laser spot. We assume a stationary state, i.e. the laser is always on at a constant power. When the laser heats the sample at the center of the hole, the heat will dissipate radially, first along the suspended region (inside the hole) of the sample and later on through the supported region (outside the hole). The temperature difference, $\Delta T(r) = T(r) - T_0$ will vary from the maximum value at r = 0 to $\Delta T = 0$, far away from the center, T_0 being usually room temperature.

Substituting the term for heat source in Eq (2) by the Gaussian beam profile, the heat equation in the suspended region becomes [12]:

$$\frac{\kappa}{r}\frac{d}{dr}\left[r\frac{d\Delta T_1(r)}{dr}\right] + \frac{P_{abs}}{d\pi r_0^2}e^{-r^2/r_0^2} = 0, r < R$$
(10)

 P_{abs} is the absorbed power, r_0 is half of the objective resolution,

$$r_0 = \frac{\lambda}{\pi NA} \tag{11}$$

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 λ being the laser wavelength and *NA* the numerical aperture of the objective. In Ref [12] authors fit the Airy profile with a Gaussian profile for a 50× and a 100× objective to deduce r_0 averaging from the Airy profile. The Airy profile can be cleaned up using a spatial filter.

In the supported region, the heat-diffusion equation is

$$\frac{\kappa'}{r}\frac{d}{dr}\left[r\frac{d\Delta T_2(r)}{dr}\right] - \frac{G_b}{d}\Delta T_2(r) = 0, \quad r \ge R$$
(12)

where G_b is the thermal boundary conductance between the flake and the substrate, and we have assumed that the laser spot is completely confined to the suspended region. The thermal conductivity in the supported region can be different from the suspended region in the general case. The general solution of Eq (10) is

$$\Delta T_1(r) = \frac{P_{abs}}{4\pi k d} \operatorname{Ei}\left(-r^2/r_0^2\right) + C_1 \ln \frac{r}{r_0} + C_2 \tag{13}$$

in terms of the exponential integral Ei(z) and a natural logarithm, while the solution of Eq (13) is

$$\Delta T_2(r) = C_3 I_0(\beta r) + C_4 K_0(\beta r) \tag{14}$$

where $\beta = \sqrt{G_b / \kappa' d} = (\kappa' dR_b)^{-1/2}$, R_b being the boundary resistance, and $I_0(z)$ and $K_0(z)$ are Bessel functions of the first and second kind, respectively. The constants C_1 , C_2 , C_3 and C_4 can be obtained by applying four boundary conditions:

$$\left. \frac{d\Delta T_1}{dr} \right|_{r=0} = 0,\tag{15}$$

since the temperature must have a maximum at r = 0, the center of the Gaussian spot,

$$\Delta T_1(R) = \Delta T_2(R),\tag{16}$$

in the limiting regions between the suspended and the supported region the temperature variation must be continuous,

$$\kappa \frac{d\Delta T_1}{dr}\Big|_{r=0} = \kappa' \frac{d\Delta T_1}{dr}\Big|_{r=R'}$$
(17)

since the heat current must also be continuous (κ' being the thermal conductivity in the supported region). Therefore, the last condition is

$$\lim_{n \to \infty} \Delta T_2(r) = T_2(r \to \infty) - T_0 = 0.$$
⁽¹⁸⁾

since far away from the spot, the temperature must tend to T_0 . Applying the boundary conditions to Eqs (13) and (14), we have

$$\Delta T_1(r) = \frac{P_{abs}}{4\pi\kappa d} \left\{ \left[\operatorname{Ei}\left(-\frac{r^2}{r_0^2}\right) - \operatorname{Ei}\left(-\frac{R^2}{r_0^2}\right) - 2\ln\frac{r}{R} \right] + \frac{2\kappa}{R} \sqrt{\frac{d}{g\kappa'}} \frac{K_0(\beta R)}{K_1(\beta R)} \left(1 - e^{-R^2/r_0^2}\right) \right\}$$
(19)

where g is the interface boundary resistance in the supported region, and

$$\Delta T_2(r) = \frac{P_{abs}}{4\pi\kappa R} \sqrt{\frac{d}{g\kappa'} \left(1 - e^{-R^2/r_0^2}\right) \frac{K_0(\beta r)}{K_1(\beta R)}}.$$
(20)

Since

$$\Delta T_1(R) = \Delta T_2(R) = \frac{P_{abs}}{2\pi dR} \sqrt{\frac{d}{g\kappa'} \left(1 - e^{-R^2/r_0^2}\right) \frac{K_0(\beta R)}{K_1(\beta R)}}$$
(21)

We can substitute the last term in Eq (19) by $\Delta T_1(R)$ obtaining

$$\Delta T_1(r) = \Delta T_1(R) + \frac{P_{abs}}{4\pi\kappa d} \left[\operatorname{Ei}\left(-\frac{r^2}{r_0^2}\right) - \operatorname{Ei}\left(-\frac{R^2}{r_0^2}\right) - 2\ln\frac{r}{R} \right]$$
(22)

This expression gives us the temperature profile in the suspended region. But experimentally we do not have access to the temperature profile, thus we will calculate the average temperature (T_{spot}) in the spot region

integrating the Gaussian beam, assuming $r_0 \ll R$, as follows

$$T_{spot} = \frac{\int_0^R T(r) \ e^{-r^2/r_0^2} r dr}{\int_0^R e^{-r^2/r_0^2} r dr}$$
(23)

here we have integrated until r=R, but actually if, $R \ge 3r_0$, the integrals can be extended to infinity with an error of the order of 10^{-4} . In that case,

$$\int_{0}^{\infty} e^{-r^{2}/r_{0}^{2}} r dr = \frac{r_{0}^{2}}{2}.$$
(24)

On the other hand,

$$\int_{0}^{\infty} e^{-x^{2}} [\operatorname{Ei}(-x^{2}) - \ln x^{2}] x dx = \frac{1}{2} [\gamma - \ln 2]$$
(25)

where γ is the Euler's constant. The full expression for the average spot temperature is

$$\Delta T_{spot} = \Delta T(R) + \frac{P_{abs}}{4\pi\kappa d} \left[-0.115932 + 2\ln(R/r_0) - \text{Ei}(-R^2/r_0^2) \right]$$
(26)

The thermal resistance of the flake, R_{th} , can be defined as the temperature difference between the spot and the temperature at the hole radius divided by the heat flow rate Q:

$$R_{th} = \frac{T_{spot} - T(R)}{Q} = \frac{\ln(R/r_0)}{2\pi\kappa d} \left[1 + \frac{\gamma - \ln 2 - \text{Ei}\left(-\frac{R^2}{r_0^2}\right)}{2\ln(R/r_0)} \right]$$
(27)

This expression is the same as that given by Eq (9), but here r_0 is the spot radius and R the radius of the holes, with a small correction factor given by the square brackets. For a typical value of $R/r_0 \sim 4$, the term into brackets in Eq (27) gives 0.958 approximately. Assuming that the term into bracksts in Eq (27) is 1, the thermal conductivity κ can be calculated with a 4% error as,

$$\kappa = \frac{\ln(R/r_0)}{2\pi dR_{th}} = \frac{\ln(R/r_0)}{2\pi d} \frac{\Delta P}{\Delta T}$$
(28)

where we have substituted the heat flow Q of Eq (7) by the laser heat flow P. The radius r_0 of the laser spot can be obtained by the resolution of the objective, the sample thickness and the radii of the holes are known quantities, thus we only need to obtain experimentally the thermal conductance, $G_{th} = P/\Delta T$, where $\Delta T = T_{spot}$ -T(R).

To avoid the knowledge of the absolute temperature and power, we can proceed in the following way: First, we measure the phonon shift as a function of temperature and from the plot $\Delta \omega = \omega(T) - \omega(T_0)$, we extract the slope,

$$\chi_T = \frac{\partial \omega_0}{\partial T} \tag{29}$$

Next, we measure the phonon shift as a function of power, $\Delta \omega = \omega(P) - \omega(P_0)$, where $\omega(P_0)$ is the phonon frequency without the laser beam and extract the slope,

$$\chi_P = \frac{\partial \omega_0}{\partial P} \tag{30}$$

The thermal conductance can be written as

$$G_{th} = \chi_P / \chi_{T_{t}}, \tag{31}$$

and inserting the value of G_{th} in Eq (28), we can obtain the thermal conductivity.

3 Phonon anharmonicity

We would like to remember some basic physical concepts since we have observed in many articles wrong conclusions, made probably by people not very familiar with Raman spectroscopy. What is thermal expansion? The definition of the linear thermal expansion coefficient α is

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$$\alpha = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_P = \frac{1}{3V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{3} \alpha_V$$
(32)

written in terms of the volume expansion coefficient α_V , more generally used. Thermal expansion tells us how the lattice parameter of the crystal changes with temperature. In an anisotropic material the linear expansion coefficient will be different in different directions, but let us assume that α_V is a scalar for the sake of simplicity. We have to pay attention to the fact that the thermal expansion, by definition, is calculated at constant pressure. In many articles the thermal expansion is used to calculate the stress in the sample and from the stress, the contribution to the Raman shift using the phonon deformation potentials. Thermal expansion has nothing to do with stress, the change in the volume is due to lattice vibrations. The lattice vibrations, in general, produce an expansion of the solid since they need more space to vibrate at high temperatures (at low temperatures the thermal expansion is negative due to the contribution of acoustic phonons, which have a negative Grüneisen parameter).

The variation of the phonon frequency with the volume is given by the Grüneisen parameter

$$\gamma = -\frac{\partial \ln \omega}{\partial \ln V} = -\frac{1}{\alpha_V} \left(\frac{\partial \ln \omega}{\partial T} \right)_P \tag{33}$$

We would like to emphasize that the Grüneisen parameter is also given at constant pressure. The contribution to the thermal expansion to the temperature is

$$\omega(T) = \omega(0) \ e^{-\gamma \int_0^1 \alpha_V dT}$$
(34)

We have to add this contribution to the anharmonic terms coming from three and four-phonon processes. As mentioned at the end of Sec. 2, we have to measure the change in the phonon frequency with the temperature to obtain χ_T , but it is important to know the origin of the shift. The shift is due to anharmonic effects, including thermal expansion.

4 Errors and uncertainties

There are many uncertainties in the measurement of the thermal conductivity using Raman thermometry. Beechem *et al* [16] discuss the validity of the models used in the analysis of the thermal conductivity in suspended wafers by comparing them with a finite elements numerical simulation. Although they do not take into account some possible important sources of error, like convection losses or radiation, they claim that important errors can be generated by averaging the temperature in the suspended region or neglecting the mechanical stress produced by laser heating. If present, biaxial stress can introduce certainly some inaccuracies, which are actually difficult to evaluate. Not only temperature, but also stress produce phonon shifts. The phonon shift with stress is given by the phonon deformation potentials. In MoSe₂ for instance, the in-plane phonon deformation potential is $2\tilde{a} \approx 233$ cm⁻¹ to both A_{1g} and E_{2g}¹ [24]. The bulk modulus of MoSe₂ must be reasonably smaller than that of Si (*B* = 98 GPa), thus the shift due to the possible strain due to the attachment of the flake in the supported region will be smaller than 0.02 cm⁻¹, thus even if the sample is attached in the supported region, the influence of stress due to the temperature variation of the suspended region is negligible.

Unfortunately, the authors of Ref [16] were not familiar with phonon renormalization effects, the phonon shift is due to the third and quartic terms in the potential energy of the lattice (three and four phonon processes, including thermal expansion) and has nothing to do with the stress. The problem is that wrong arguments (the mentioned article has at present 250 citations) are spread among the readers and at this point, an important number of young researchers could be taken the thermal expansion as a source of stress. Either, there was no referee or the referee had no much idea about Raman spectroscopy. The paper probably deserves a comment to stop the dissemination of the wrong concepts given in this work.

In a recent work of D S Reig *et al* [21] a careful analysis of the procedure to obtain the thermal conductivity in bulk and in the monolayer limit using Raman thermometry has been performed. Rewriting our Eq (2) including the convection and radiation (in red) losses,

$$C\frac{\partial T}{\partial t} = \kappa \nabla^2 T + S - \frac{2h_c \Delta T}{d} - \frac{8\sigma_{SB}T^3 \Delta T}{d}$$
(35)

where the additional factor of 2 comes from the number of surfaces of the flake. In the simulations made in Ref [21], even at a $\Delta T = 200$ K, the error in the thermal conductivity due to thermal radiation (radiation losses) is smaller than 0.1% for 1 ML and ten times smaller for 2 ML. Of course completely negligible for thicker samples. The experiments were performed at room temperature. At much higher temperatures, for instance 900 K, the error will be smaller than 3% for 1 ML and negligible for thicker samples. The second source of errors are the convection losses.

The heat losses due to convection depend on the material. In the case of $MoSe_2$ [21], the losses by convection seems to be important in samples under 10 ML. In a 1 ML sample, the apparent thermal conductivity $\kappa_{app} \approx 150 \text{ Wm}^{-1}\text{K}^{-1}$, while the thermal conductivity measured in vacuum conditions is $\kappa_{vac} \approx 20$ $\text{Wm}^{-1}\text{K}^{-1}$, nearly one order of magnitude higher. For 3 ML, the apparent thermal conductivity is three times higher and after 10 ML the difference can be neglected. Thus, the measurement of the thermal conductivity in the ML limit must be performed under vacuum. But we can turn the interpretation around, as Reig *et al* do in [21]. It is also important to measure the effective (apparent) thermal conductivity since this is the thermal conductivity which will play a role in devices. The convection losses are basically due to the coupling of the atomic vibrations at the surface of the materials with that of the air molecules. Since the vibrational modes of the air molecules do not have the same frequency than that of the solid, the penetration depth of such vibrations can be limited to one monolayer. In our opinion, it makes no sense to talk about convection in the case of a monolayer. The convection must be reserved for the surface of a material with a given volume and as we can check in the discussion given in Ref [21], when we have a volumetric material the convection losses are negligible. In the case of 1 ML instead of convection it makes more sense to talk about the interaction of an atomic layer with the air.

5 Comments on the experimental setup

In this section we will describe a standard experimental setup for the measurement of the thermal conductivity of semiconductor flakes by means of opto-thermal Raman spectroscopy (OTRS). As in a standard Raman experiment the crucial points are a laser and a Raman spectrometer. Since, we will need a small size spot, a microscope objective is also needed. Let us discuss all the elements needed for the experiment.

• Since we will need to carry on experiments at different laser powers, a stabilized laser with variable power will be needed. Failing to that, a laser with fixed power of the order of 100 mW and a set of neutral density filters (or a filter wheel) can be used instead. The wavelength of the laser depends on the sample, in general a solid state laser in the visible region has been used in the literature [25,26,28,29,31-36,41,42]. A non-polar phonon must be selected to avoid additional shifts due to resonance effects.

• A microscope objective $100 \times$ with a hight NA of 0.9 or 0.95 must be used to have a small spot radius r_0 . If a cryostat is used, either because we want to do the measurements under vacuum or as a function of temperature, a long working distance (LWD) objective must be used. The objectives with longer WD in the market are that of Mitutoyo. For instance, an M Plan Apo SL 100× Mitutoyo objective has a WD of 13 mm, a NA of 0.55 and 500 nm resolution ($r_0 \sim 250$ nm). Other objectives in the market are the Olympus SLMPLN 100× (WD =7.6 mm, NA = 0.6 and 560 nm resolution) or, if we do not need very long WD, an EPLE 100×, from Opto-Sigma (WD = 2 mm, NA = 0.8, 300 nm resolution). As soon as we decrease the working distance, the NA and resolution increases. For instance, the Mitutoyo M Plan Apo HR 100× objective has a small working distance of WD =1.3 mm, but with NA= 0.9, the resolution goes down to 300 nm.

• A Raman system with a spectral resolution better than 1 cm^{-1} must be used. A single spectrometer with at least 500 mm focal length, an edge filter and a CCD camera is the basic setup for the Raman measurements. If we know the anharmonic phonon parameters, we only need to know the phonon shift as a function of the laser power. Otherwise we need also to measure the phonon shift with temperature varying the temperature in a wide range, from 300 to 400 K for instance. This can be done in air or in vacuum compatible high temperature Linkam stage for instance, suitable for microscopy. If we want to control the temperature by measuring the anti-Stokes/Stokes ratio we have to replace the edge by a notch filter.

• A substrate with high thermal conductance and holes at least 5 times the microscope resolution. In Ref. [21] they recommend to coat the substrate with Au to improve the thermal contact in the supported region. The temperature in the supported region decreases by a factor of 3 when they use gold instead on Si_3N_4 , since the heat can be dissipated very well through the gold [21].

• For a few monolayers (less than 10), if we are interested in the real value of the thermal conductivity, we have to perform the experiment under vacuum conditions. In this case, we can use either the same high temperature stage mentioned above or a cryostat. In case, we are not interested in κ_{vac} , but the thermal conductivity in air, which will be suitable for a device testing, κ_{air} .

• Finally, if we are interested in measuring the thermal conductivity as a function of temperature we will need a micro-cryostat and/or a high temperature stage.

6 Thermal conductivity of 2Dmaterials

In Table 1, we have listed a set of 2D materials whose thermal conductivity has been meassured using the method discussed in this work. We have included the space group of the material, the thickness of the flakes, the value of the thermal conductivity and the corresponding reference. In the case of strictly one dimensional materials as graphene and a layer of Te, the space group is that of the bulk (graphite and bulk Te). In the case the material has also been measured by other methods, the corresponding value has also been included. All values presented in Table 1 correspond to room temperature and have been measured in air conditions. The highest value of κ is that of graphene, 2500 Wm⁻¹K⁻¹, although other methods give slightly hiher values.

In Ref [25], they measured the thermal conductivity of MoS_2 and $MoSe_2$ using the OTRS method. From the supplementary information, it seems that the substrate consists of Si, 280 nm of SiO₂ on top, and coated with 10 nm Au. The holes made in the substrate have a diameter of 4 µm and a depth of 1.8 µm. Once the laser is transmitted, it is reflected at the bottom of the hole, giving rise to an extra heating component which they estimate to be ~ 5% of the transmitted power. The spot of the laser is estimated to be 460 and 620 nm corresponding to a 100× and 50× microscope objectives, respectively. A 532 nm laser was used in the MoS₂ experiment while the MoSe₂ was measured with a He-Ne laser (633 nm). The values of the thermal conductivity reported, different for the suspended and supported regions, have large uncertainties. At room temperature, the thermal conductivity of 1 ML MoS₂ is 84±17 WK⁻¹m⁻¹ in the suspended region and 55±20 WK⁻¹m⁻¹ in the supported one. For 1 ML of MoSe₂, it decreases to 59±18 WK⁻¹m⁻¹ in the suspended region and to 24±11 WK⁻¹m⁻¹ in the supported region. In the case of 2 ML of MoS₂ they obtained a value of 77±25 WK⁻¹m⁻¹ in the suspended region and 35±7 WK⁻¹m⁻¹ in the supported one. Additionally, they have measured the thermal conductivity of MoS₂ in the suspended region at 500 K, providing a value of 66±16 WK⁻¹m⁻¹ for 1 ML and 29±10 WK⁻¹m⁻¹ for 2 ML.

Yu *et al* [18] measured the thermal conductivity of MoS_2 , WS_2 and WSe_2 on Si/SiO₂ or quartz substrates, but without any information on the depth of the holes. As mentioned in Ref [25], if the holes are not very deep, part of the laser beam can be reflected at the bottom of the hole and again heat the

sample increasing the error in the measurement. The holes have diameters between 1.8 and 6.5 µm. They found an increasing thermal conductivity with the hole radius, but they select as the most confident value corresponding to a hole of 4 µm diameter. The thermal conductivity decreases with the number of layers, probably due to convection effects (see previous section) from 1 to 4 layers. The values for 1 to 4 layers in MoS₂ are 55, 39, 42 and 37 Wm⁻¹K⁻¹, respectively as extracted from Fig 3(b). However, they give a value of $32.5 \pm 3.4 \text{ Wm}^{-1}\text{K}^{-1}$, corresponding to a hole of 1.8 µm diameter to compare with other experimental results from the literature. Considering 4 µm diameter as a reasonable value for the hole diameter, the thermal conductivities are 45, 50 and 55 Wm⁻¹K⁻¹ for MoS₂, WSe₂ and WS₂, respectively, as extracted from Fig 3(c). N Peimyoo et al [28] have also measured the thermal conductivity of WS₂. A WITEC Raman system and a Linkam microscopic stage for LN_2 was used to measure the shift of the phonon with temperature. A long WD 50 \times objective with a numerical aperture of 0.55 was used in that case. The laser power was kept below 40 μ W to avoid laser heating during the measurements as a function of T. However, the measurements as a function of power were performed in air conditions with a $100 \times$ objective having a NA = 0.95. The thermal conductivity of WS₂ was estimated to be 32 and 53 $Wm^{-1}K^{-1}$ for the monolayer and the bilayer, respectively.

| Table 1 | . In-plane therr | nal conductivity of 2 | 2D materials, measu | red by the OTRS method at roo | om temperat |
|---------|---------------------------------|-----------------------|---------------------|--|-------------|
| | Material | Space Group | Thickness | $\kappa (\mathrm{Wm}^{-1}\mathrm{K}^{-1})$ | Ref. |
| | Graphene | P6 ₃ mmc | 1 ML | $2500{}^{+1100}_{-1050}$ | [12] |
| | MoS_2 | P6 ₃ /mmc | 1/2 ML | $84 \pm 17~/~77 \pm 25$ | [25] |
| | | | 1/2 ML | 55 ^{a*} / 39 ^{a*} | [18] |
| | | | 1/2 ML | $(13.3\pm1.4~/~15.6\pm1.5)^{vac}$ | [26] |
| | MoSe ₂ | P6 ₃ /mmc | 1/2 ML | $59 \pm 18 \ / \ 42 \pm 13$ | [25] |
| | MoTe ₂ | P6 ₃ /mmc | 17 nm | 3.72 ± 0.26 | [27] |
| | WS ₂ | P6 ₃ /mmc | 1/2 ML | 32/52 | [28] |
| | | | 1 ML | 68 ^a | [18] |
| | WSe ₂ | P6 ₃ /mmc | 1 ML | 62 ^a | [18] |
| | WTe ₂ | Pmn2 ₁ | 50 nm | 4.45^{zz} and 4.10^{ar} | [29] |
| | PtS_2 | P3m1 | 4 nm | 85.6 ± 7.7 | [30] |
| | PtSe ₂ | P3m1 | 4.5 nm | 40.4 ± 4.7 | [30] |
| | SnS_2 | P3m1 | 45 – 171 nm | 8.3-11.8 | [31] |
| | SnSe ₂ | P3m1 | 5/15 ML | $1.80 \pm 0.05 \ / \ 2.90 \pm 0.17$ | [32] |
| | PdSe ₂ | Pbca | 1.62 nm | 10.95 ^x and 15.58 ^y | [33] |
| | CrI ₃ | C2/m, R3 | 1 ML | 4.4 ± 1.4 | [34] |
| | Sb ₂ Te ₃ | R 3 mH | 115 nm | ~ 10 | [35] |
| | h-BN | P6 ₃ /mmc | 1/3 ML | $751 \pm 340 \ / \ 602 \pm 247$ | [36] |
| | | | 5/11 ML | 250 ^{1a} / 360 ^{1a} | [37] |
| | CrOCl | Pmmn | 2 nm | 392 ± 33^{zz} and 129 ± 3^{ar} | [38] |
| | | | 50 nm | 1017 ± 46^{zz} and 237 ± 11^{ar} | [38] |
| | FePS ₃ | C2/m | | $1.35\pm 0.32~/~2.7\pm 0.3^2$ | [39] |
| | MnPS ₃ | C2/m | | 6.3 ± 1.7^2 | [39] |

| 2H-TaSe ₂ | P6 ₃ /mmc | 45 nm / Bulk | 9 / 16 | [40] |
|----------------------|--|--------------|--|------|
| 2D Te | P3 ₁ 21, P3 ₂ 21 | 15 nm | $0.6^{\perp} \text{ and } 1.6^{\parallel}$ | [41] |
| | | 100 nm | $1.7^{\perp} \text{ and } 2.5^{\parallel}$ | [41] |
| BP | Cmce | 9.5 nm | $\sim 20^{zz}$ and $\sim 10^{ar}$ | [42] |
| | | 15 nm | $\sim 40^{zz}$ and $\sim 20^{ar}$ | [42] |

*see text, avalues extracted from graph, vacmeasurements taken under vacuum conditions, ^{zz}thermal conductivity in the zig-zag direction (κ_{az}), ^{ar}thermal conductivity in the armchair direction (κ_{arm}), ^xthermal conductivity along x (κ_x), ^y thermal conductivity along y (κ_y). [⊥]cross-chain thermal conductivity, [⊥]thermal conductivity along-chain, ¹ κ obtained with the micro-bridge method, ² κ obtained through time-resolved MOKE.

Bae *et al* [26] have also measured the thermal conductivity of MoS₂. They use a Si/SiO₂ substrate coated with gold and patterning holes from 2-6 μ m diameter and 5 μ m in depth. The measurements were carried out in vacuum conditions. The values are 13.3 ± 1.4, 15.6 ± 1.5 and 43.4 ± 9.1 Wm⁻¹K⁻¹ in the monolayer, bilayer and multilayer cases, respectively [26]. The obtained values of the thermal conductivity with the number of layers increase and is consistent with the work of S Reig *et al* [21].

Zhang *et al* [31] have measured the thermal conductivity of mono- and polycristalline SnS₂. The thermal conductivity of monocrystalline SnS₂ changes from 8.3 to 11.8 Wm⁻¹K⁻¹ for thicknesses between 45 nm and 171 nm, increasing with the number of layers. The thermal conductivity of 16-190 nm thick SnSe₂ has also been measured using OTRS and TDTR [43]. The in-plane thermal conductivity varies from, $\kappa_{\parallel} = 6.45 \pm 0.71$ Wm⁻¹K⁻¹ for the thickest film (190 nm) to $\kappa_{\parallel} = 2.54 \pm 0.31$ Wm⁻¹K⁻¹ for the thinnest film (16 nm), which corresponds to a reduction by a factor 2.5. A similar reduction is found for κ_{\perp} , the value drops from 0.83 ± 0.12 Wm⁻¹K⁻¹ for d = 190 nm to 0.28 ± 0.05 Wm⁻¹K⁻¹ for d = 16 nm. The thermal conductivity increases with the number of layers, as in previous works. The thermal conductivity of CrI₃ flakes has been measured by Opto-thermal Raman scattering and time domain foto reflectance by Gish [34]. The values obtained are $\kappa_{\parallel} = 4.4 \pm 1.4$ and $\kappa_{\perp} = 0.32 \pm 0.11$ Wm⁻¹K⁻¹. CrI₃ is a ferromagnetic semiconductor.

Cai *et al* [36] have measured the thermal conductivity of boron nitride (BN) by means of optothermal Raman scattering. The average values of κ for 1, 2 and 3 ML of BN were 751 ± 340, 646 ± 242, and 602 ± 247 Wm⁻¹K⁻¹, respectively at room temperature. These values are not consistent with many other values found in the literature, but they agree with the DFT calculations performed in Ref [36].

Layered CrOCl is an anti-ferromagnetic insulator with low level symmetry crystal structure (space group Pmmn) and atomic level flatness. X Zheng *et al* [38] have measured the thermal conductivity of suspended few layers flakes (2-50 nm) by means of optothermal Raman scattering. The thermal conductivity along the zig-zag direction was $\kappa_{zz} = 1017 \pm 46 \text{ Wm}^{-1}\text{K}^{-1}$ for 50 nm thickness and decreased sharply to $\kappa_{zz} = 392\pm33 \text{ Wm}^{-1}\text{K}^{-1}$ for 2 nm. The thermal conductivity along the armchair direction varies from, $\kappa_{arm} = 237 \pm 11 \text{ to } \kappa_{arm} = 129 \pm 3 \text{ Wm}^{-1}\text{K}^{-1}$. The anisotropy ratio goes from 3 to 4.5. They also show the value of κ_{arm} as a function of temperature, going from 100 Wm⁻¹K⁻¹ at 170 K to 45 Wm⁻¹K⁻¹ around 370 K.

PtS₂ and PtS₂ are noble transition metal dichalcogenides with applications in opto electronics [30]. They belong to the $P\overline{3}$ m1 space group. The resulting thermal conductivities are 85.6 ± 7.7 and 40.4 ± 4.7 Wm⁻¹K⁻¹ for 4 nm PtS₂ and 4.5 nm PtS₂, respectively.

The thermal conductivity of thin flakes from FePS₃ and MnPS₃ single crystals have been measured by optothermal Raman scattering and time resolved MOKE. These are antiferromagnetic semiconductors crystallizing in the C2/m space group. They [39] do not give information on the flake thickness. The thermal conductivity of FePS₃ measured with OTRS is $\kappa_{\parallel} = 1.35 \pm 0.32$ Wm⁻¹K⁻¹, while TR-MOKE gives values for $\kappa_{\perp} = 0.85 \pm 0.15$ and $\kappa_{\parallel} = 2.7 \pm 0.3$ Wm⁻¹K⁻¹. The in-plane conductivity can be compared with that measured by OTRS. Using TR-MOKE, Kargar *et al* [39] have also measured the thermal conductivities of MnPS₃, giving the values of $\kappa_{\perp} = 1.1 \pm 0.2$ and $\kappa_{\parallel} = 6.3 \pm 1.7$ Wm⁻¹K⁻¹. In black phosphorus, the thermal conductivity values, $\kappa_{zz} \sim 20 \text{ W.K}^{-1}\text{m}^{-1}$ and $\kappa_{arm} \sim 40 \text{ W.K}^{-1}\text{m}^{-1}$ for films thicker than 15 nm, are reduced by a factor of two in the measurement of a 9.5 nm thick film ($\kappa_{zz} \sim 10 \text{ W.K}^{-1}\text{m}^{-1}$ and $\kappa_{arm} \sim 20 \text{ W.K}^{-1}\text{m}^{-1}$) [42]. All the measurements were taken in a nitrogen atmosphere.

Yan *et al* [40] have measured the thermal properties of 2H-TaSe₂. At room temperature, the thermal conductivity decreases from the bulk value, $16 \text{ Wm}^{-1}\text{K}^{-1}$ to $9 \text{ Wm}^{-1}\text{K}^{-1}$ for a 45 nm thick flake.

7 Conclusions

The most confident technique to measure the thermal conductivity of 2D materials in a few layers limit is based on Raman spectroscopy and called opto-thermal Raman technique or Raman thermography. In this technique the sample is placed on a substrate with holes in such a way that there is a section of the sample on top of the hole and the remaining part on the substrate (supported part). The diameter of the holes must be 4-5 times the size of the laser spot and they must be deep enough to avoid reflection from the bottom of the hole. We have discussed the principles of the method, the ideal conditions to obtain confident results, the main sources of errors and the main results found in the literature.

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