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Original scientific paper

CALCULATION OF THERMAL CONDUCTIVITY FOR CRYSTALLINE NANOSTRUCTURES

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ABSTRACT

We have introduced a theory for the calculation of thermodynamic characteristics for some characteristic nanostructures (ultrathin films and superlattices), using the adapted method of two-time temperature Green's functions. In this paper, he has determined the coefficient of thermal conductivity using the definition of free energy and then compared their temperature dependence to the thermal conductivity behavior of the bulk structures. For the observed nanostructures, the thermal conductivity coefficient values are almost equal at low temperatures, but at the same time, significantly lower than the bulk sample values. That result could be useful for the possible achievement of better superconducting conditions in the observed compound nanostructures.

Keywords: ultrathin films, superlattices, phonons, thermodynamics, thermal conductivity

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1. INTRODUCTION

Elementary particles – mechanical oscillations – phonons are a subsystem that is always present when analyzing the conducting, semiconducting, or dielectric properties of the system. Accordingly, we will first analyze the kinetics of mechanical oscillations in nanoscopic–ultrathin films, which can be considered as a basis for investigating other properties of more complex nanostructures. In a way, this work represents a generalization of the previous research [1–6].

We will start with the definition expression for the coefficient of thermal conductivity [7,8]:

$$\kappa = D\,C\,\rho_M \qquad (1.1)$$

where D is the diffusion coefficient, C – specific heat, and ρ_M is the mechanical density of the observed structure. The diffusion coefficient D (strictly, it is the diagonal matrix element of diffusion tensor D_{ij}) will be found by the Kubo formula [7]. The temperature dependence of nanostructure density will be determined by the two-time, temperature-dependent Green's function method [9]. Using this method one can find the internal energy and the average value of the square of molecular displacements.

All analyzes will be calculated regarding the presence of specific boundary conditions on its surfaces, which are responsible for the appearance of unusual effects and changes in the basic properties of these structures [6].

2. CALCULATION OF THE DIFFUSION COEFFICIENT

To determine the diffusion coefficient, we will start with the Kubo formula [7,8]:

$$D_{ij}=\frac{1}{\beta}\int_0^\infty \mathrm{e}^{-\varepsilon t}\int_0^\beta d\lambda\left\langle \hat{v}_i(-i\eta\lambda)\hat{v}_j(t)\right\rangle \approx \lim_{t_0\to\infty}\int_0^\infty \mathrm{e}^{-\varepsilon t}\langle \hat{v}_i(0)\hat{v}_j(t)\rangle dt\,, \tag{2.1}$$

where $\hat{v}_i$ and $\hat{v}_j$ (*i,j = x,y,z*) are the velocity operators in Heisenberg representation, ε is the perturbation parameter and the averages will be taken over the great canonical ensemble. We will find the correlation function $\langle \hat{v}_i(0)\hat{v}_j(t)\rangle$ through Green's function $\langle\langle p_i(t)\big| p_j(0)\rangle\rangle$, which represents the components of the molecular momentum.

The Hamiltonian of the phonon subsystem of a superlattice with two motifs a and b (two ultrathin films) taken in harmonic and nearest neighbor's approximation [9], can be written as follows:

$$H=T+V_P+V_B;\quad T=\sum_{n,\alpha}\sum_{n_l=0}^{n_a-1}\frac{\left[p^{(a)}_{n,n_l,\alpha}\right]^2}{2M_a}+\sum_{n,\alpha}\sum_{n_l=n_a}^{n_a+n_b-1}\frac{\left[p^{(b)}_{n,n_l,\alpha}\right]^2}{2M_b}; \tag{2.2}$$

where $M_{a/b}$ are the masses of molecules in first/second ultrathin films, $V_{P/B}$ are the potential energies of surface and bulk terms, $p\equiv M\dot{u}$ (u are molecular displacements), and $n_{a/b}$ are numbers of molecules in corresponding motive. Boundary conditions will be taken into account during the formation of a system of equations defining Green's function of the system. We have determined the following Green's function, which will be written in the next form: Because of valid relation: $p_i = M\,v_i$; $vi = \mathrm{d}u_i / \mathrm{d}t$, in the expression determining this function, appears the second Green's function of a type $<< u_{n_x n_y f}(t)\big|\ u_{n_x n_y f}(0) >>$ [10]. In this way, the correlation function of the Green's function is given by a general formula [11,12]:

$$< p_f(t)p_f(0) >=\lim_{\varepsilon\to+0}\int_{-\infty}^{+\infty} d\omega\ \mathrm{e}^{-i\omega t}\ \frac{G_f(\omega+i\varepsilon)-G_f(\omega-i\varepsilon)}{\mathrm{e}^{\eta\omega/\theta}-1}\,. \tag{2.3}$$

Green's function can be expressed as a sum of elementary fractions [10]. In this way, we obtain the correlation function (2.3), i.e. corresponding velocity correlation function:

$$< v_f(t)v_f(0) >=\frac{\eta C_H}{M^2\omega_k}\left(\frac{\mathrm{e}^{-i\omega_k t}}{\mathrm{e}^{\eta\omega_k/\theta}-1}-\frac{\mathrm{e}^{i\omega_k t}}{\mathrm{e}^{-\eta\omega_k/\theta}-1}\right). \tag{2.4}$$

By the general formula (2.2) the diffusion coefficient is given by:

$$D_{ii}(k)=\left|\frac{\eta C_H}{M^2\omega_k}\int_0^\infty\left(\frac{\mathrm{e}^{-i\omega_k t}}{\mathrm{e}^{\eta\omega_k/\theta}-1}-\frac{\mathrm{e}^{i\omega_k t}}{\mathrm{e}^{-\eta\omega_k/\theta}-1}\right)dt\ \right|=\frac{\eta C_H}{M^2\omega_k^2}\,. \tag{2.5}$$

It is seen that the phonon diffusion coefficient of the superlattice, as well as that of the bulk, does not depend on temperature [13].

3. THERMODYNAMIC BEHAVIOUR OF SUPERLATTICE

The internal energy of the system is given by the standard formula [11-13]:

$$U_s=\frac{3}{(2\pi)^3}Na^3\int_0^{2\pi}d\varphi\int_0^{\pi}\sin\theta d\theta\int_0^{k_M}dk k^2\eta\Omega ka\left(\mathrm{e}^{\frac{\eta\Omega ak}{\theta}}-1\right)^{-1}, \tag{3.1}$$

where the phonon dispersion law is given by the basic formula: *Phonon-reduced* frequencies and intermolecular distance are expressed through the geometric mean of phonon frequencies, i.e. of intermolecular distances in separate motifs: Quantity θ is thermodynamic temperature $\theta = k_B\ T$.

After partial integration in (3.1) and introducing notations: we obtain the following expression:

$$U_s = \frac{3N}{2\pi^2}\theta\left\{6\varsigma(4)\frac{\theta^3}{(\eta\Omega)^3} - \left[a^3k_M^3 Z_1(\frac{\Delta_m}{\theta}) + 3\frac{\theta}{\eta\Omega}a^2k_M^2 Z_2(\frac{\Delta_m}{\theta}) + \right.\right.$$
$$\left.\left. + 6\left(\frac{\theta}{\eta\Omega}\right)^2 ak_M Z_3(\frac{\Delta_m}{\theta}) + 6\left(\frac{\theta}{\eta\Omega}\right)^3 Z_4(\frac{\Delta_m}{\theta})\right]\right\}. \tag{3.2}$$

Since the specific heat is given by $C_{vs} \equiv C_s = \frac{k_B}{N}\frac{\partial U}{\partial\theta}$ using (3.2), we find that:

$$C_s = \frac{3k_B}{2\pi^2}\left\{a^3k_M^3\frac{\Delta_m}{\theta}\frac{1}{1-e^{\Delta_m/\theta}} - 4a^3k_M^3 Z_1(\frac{\Delta_m}{\theta}) - 12\frac{\theta}{\eta\Omega}a^2k_M^2 Z_2(\frac{\Delta_m}{\theta}) - \right.$$
$$\left. - 24(\frac{\theta}{\eta\Omega})^2 ak_M Z_3(\frac{\Delta_m}{\theta}) + 24(\frac{\theta}{\eta\Omega})^3\left[\varsigma(4) - Z_4(\frac{\Delta_m}{\theta})\right]\right\}. \tag{3.3}$$

Temperature dependence of the thermal capacity is determined by two specific terms.

The first term is $\approx (1-e^{\Delta_m/\theta})^{-1}/\theta$ which is "responsible" for the behavior of the system at low and high temperatures. The second term containing Z-functions characterizes temperature behavior in the middle-temperature range.

Based on the results of the previous research on the phonon contribution to the thermodynamic behavior of the ultra-thin film structures [1–3], and the well-known behavior of the bulk [7,11–13], Fig. 1 shows the comparative display of the specific heat for the superlattice, ultra-thin film and the bulk structures in dependence of the reduced temperature: x=θ/Δ$_m$

From Fig. 1, one can conclude that the behavior of the thermal capacity of a superlattice in a low-temperature range is similar to bulk ones. The temperature behavior of the thermal capacity of a superlattice in a middle-temperature region is similar to film ones. The difference in these capacities is most pronounced in the high-temperature area.

Now we will approach the determination of the temperature behavior of the superlattice thermal conductivity. The expression for the dynamical density of superlattice:

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$$\rho_M = \frac{M}{<(a_0+u)^3>} = \frac{M}{<a_0^3>}\;\frac{1}{1+3<u^2><a_0^2>^{-1}} \approx \rho_0\left(1-\frac{3<u^2>}{<a_0^2>}\right) \tag{3.4}$$

The averages of squares of displacements for molecular superlattices we can find as in Debye's representation. After integration, the expression for the density becomes:

$$\rho_M = \rho_0\left(-1 + \frac{9}{2\pi^2}\frac{\eta(n_a+n_b)}{a^2\omega_D M}\frac{\theta}{\eta\Omega}\left\{(ak_M)^2 Z_1\left(\frac{\Delta_M}{\theta}\right) + 2ak_M\frac{\theta}{\eta\Omega}Z_2\left(\frac{\Delta_M}{\theta}\right) + \right.\right.$$
$$\left.\left. + 2\left(\frac{\theta}{\eta\Omega}\right)^2\left[Z_3\left(\frac{\Delta_M}{\theta}\right) - \varsigma(3)\right]\right\}\right). \tag{3.5}$$

The diffusion coefficient is given by the relation (2.5), where:

$$<\omega_k> = \frac{1}{I_0}\int_0^{2\pi}d\varphi\int_0^{\pi}\sin\theta\,d\theta\int_0^{k_M}dk\;\omega(k);\quad I_0 = \int_0^{2\pi}d\varphi\int_0^{\pi}\sin\theta\,d\theta\int_0^{k_M}dk\;k^2 \tag{3.6}$$

are the average value phonon frequencies. After elementary calculations, we obtain the diffusion coefficient:

$$D = \frac{16}{9}\frac{\eta}{M}\frac{1}{a^2k_M^2} = \frac{16}{9}\frac{\eta}{M}\left[\frac{2}{3}k_D^2 + (k_z^{\max})^2\right]^{-1} \tag{3.7}$$

Introducing notations $\theta/\Delta_m = x$ we reduce the expression (1.1) for thermal conductivity coefficient to the form:

$$\kappa = \frac{8}{3}\,\frac{\eta k_B a k_M}{\pi^2 a^3}\,J_1(x)\,J_2(x)\,, \tag{3.8}$$

where

$$\begin{aligned} J_1(x) &= \frac{\delta}{x}\,\frac{1}{1-\mathrm{e}^{\delta/x}} - 4Z_1(\delta/x) - 12\frac{x}{\delta}\;Z_2(\delta/x) - 24\left(\frac{x}{\delta}\right)^2 Z_3(\delta/x) + 24\left(\frac{x}{\delta}\right)^3 \left[\varsigma(4) - Z_4(\delta/x)\right], \\ J_2(x) &= 1 + \frac{9}{2\pi^2}\,\frac{\eta(n_a+n_b)}{a^2\omega_D M}(ak_M)^3\,\frac{x}{\delta}\left\{Z_1(\delta/x) + 2\frac{x}{\delta}Z_2(\delta/x) + 2\left(\frac{x}{\delta}\right)^2\left[Z_3(\delta/x) - \varsigma(3)\right]\right\} \end{aligned} \tag{3.9}$$

Temperature dependence of the thermal conductivity coefficient is determined by two specific terms. Similar to the expression for thermal capacity, here is the first term which is "responsible" for the behavior of the system at low and high temperatures. Also, the second term containing *Z*-functions, characterizes temperature behavior in the middle-temperature range. A graphical presentation of the dependence of the relative thermal conductivity coefficient $\kappa/\kappa_0 \equiv \lambda = 2.13\,J_1(x)\,J_2(x)$ on scaled temperature $x=\theta/\theta_D$ is given the Fig. 2.

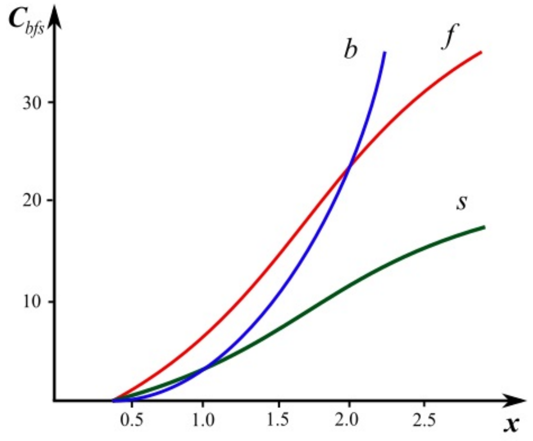

Figure 1. Specific heats of bulk (b), films (f), and superlattice (s) structures

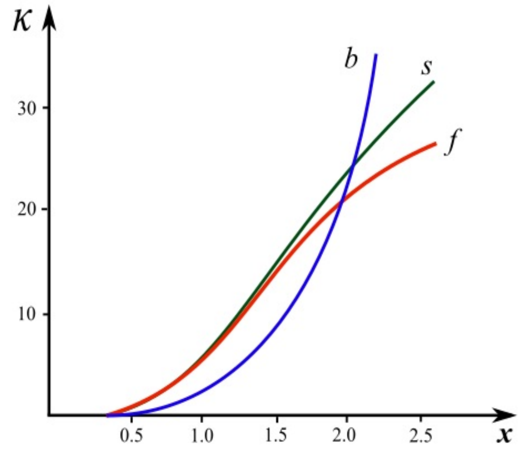

Figure 2. Conductivity coefficient of bulk (b), films (f), and superlattice (s) structures

From Fig. 2 it can be concluded that the behavior of the thermal conductivity coefficient of superlattice is similar to the ultrathin film one (it is higher than in bulk structure). The Difference is more expressive in the middle and high-temperature range. So, it can be concluded that the superlattices in the low-temperature range are somewhat better heat conductors than the bulk structures. At the same time, the heat conduction of the film is higher than in superlattices. On the other hand, in the high-temperature range superlattices are much better heat isolators than film structures and the corresponding infinite crystal structures.

As our results were obtained theoretically, we looked for experimental confirmation in the scientifically available literature. An extensive analysis of the available experimental results was carried out [14–21], of which we will in this paper present, for the sake of brevity, only a few of them. In the paper [14], the thermodynamic characteristics of micrometer SiN film structures were measured. Although these are not real nanostructures (because the thickness of these films is about 1.5 μm), film microstructures still show a similar behavior of specific heat and thermal conductivity as our theoretically obtained and predicted dependences for film structures, Fig. 3.

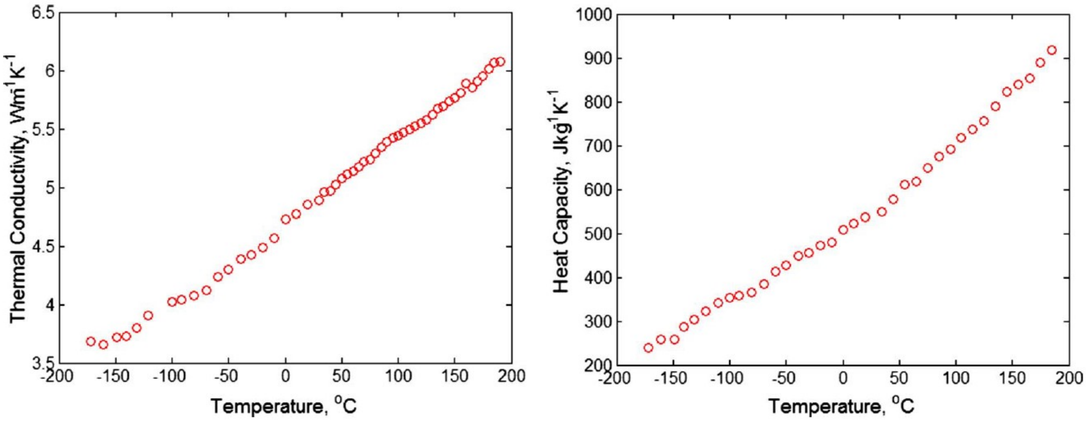

Figure 3. Thermal conductivity and heat capacity for 1.5 µm silicon nitride films [14]

Since graphene is one of the most studied materials today, and it is a true member of nano-thin (film) structures, it was justified to compare our results with the thermodynamic behavior of graphene. In the paper [15], the specific heat was measured for graphene (nano-film structure of carbon atoms), AB-stacked bilayer graphene (AB-BLG), and graphite (which represents an essential bulk structure).

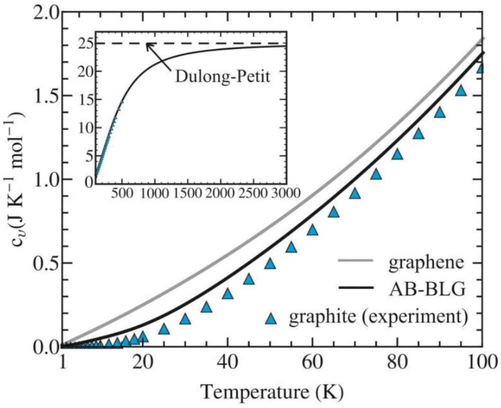

Figure 4. Phonon-specific heat capacity in graphene, AB-BLG, and graphite [15,16]

It is visible that our calculations show a similar behavior of the dependence of the specific heat on the temperature for the film structure, compared to the bulk structures, in the domain of low temperatures (i.e. on the temperatures interesting for many phenomena - such as superconductivity). Figure 4, in the frame, shows the dependence of specific heat at high temperatures, which obeys the Dulong-Petit law.

4. CONCLUSION

The results obtained here show that the thermal conductivity coefficients of the film and the superlattice at low and high temperatures are significantly lower than the thermal conductivity coefficient of the corresponding bulk structures, where the thermal coefficient dependence from temperature is T^3. This result is also practically applicable: a sandwich of several films would be a better thermal insulator than a bulk structure of the same thickness.

Here presented theoretical results are compared with experimental data [14–21]. Our theoretically predicted results are in satisfactory agreement with experimental data.

According to the Viedeman-Frantz rule, electrical conductivity is proportional to thermal conductivity. This leads to the conclusion that films and superlattices are weaker electrical conductors than bulk structures of the same material at low and high temperatures.

For future research would be interesting to evaluate the superconducting properties of observed structures. The general behavior for today's materials is that the worse conductors at the room temperature region, become the better superconductors at the low (cryogenic) temperatures region. In such a way, the ultrathin films and superlattices could be structures with high superconductivity potential, not only for the low-temperature but also for the high-temperature region.

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Conflicts of Interest

The authors declare no conflict of interest.

5. REFERENCES

[1] J. P. Šetrajčić, D. Lj. Mirjanić, S. M. Vučenović, D. I. Ilić, B. Markoski, S. K. Jaćimovski, V. D. Sajfert and V. M. Zorić, Phonon Contribution in Thermodynamics of Nano-Crystalline Films and Wires, *Acta Phys.Pol. A,* 115(2009), p.778-782

[2] J. P. Šetrajčić, V. M. Zorić, N. V. Delić, D. Lj. Mirjanić and S. K. Jaćimovski, Phonon Participation in Thermodynamics and Superconductive Properties of Thin Ceramic Films, Ch. 15, pp. 317-348, In „Thermodynamics", Ed.M.Tadashi, ISBN: 978-953-307-544-0, InTech, Vienna (Austria), 2011

[3] J. P. Šetrajčić, S. K. Jaćimovski and V. D. Sajfert, Phonon Contribution to Heat Capacitance of Nanolayered Crystalline Structures, *Mod.Phys.Lett.B,* 29(4), 1550008 [13 pages],https://doi.org/10.1142/S0217984915500086, 2015

[4] J. P. Šetrajčić, V. D. Sajfert, and S. K. Jaćimovski, Fundamental Preferences of the Phonon Engineering for Nanostructural Samples, *Rev.Theor.Sci.*, 4(2016)4, p. 353-401, doi: https://doi.org/10.1166/rits.2016.1067

[5] J. P. Šetrajčić, S. K. Jaćimovski and S. M. Vučenović, Diffusion of Phonons Through (Along And Across) the Ultrathin Crystalline Films, *Physica A,* 486(2017)5, p. 839-848, doi: https://doi.org/10.1016/j.physa.2017.06.003

[6] J. P. Šetrajčić, D. I. Ilić, and S. K. Jaćimovski, The Influence of the Surface Parameter Changes onto the Phonon States In Ultrathin Crystalline Films, *Physica A*, 496(2018), p. 434-445,https://doi.org/10.1016/j.physa.2017.12.138

[7] R. J. Kubo, Statistical-Mechanical Theory of Irreversible Processes. II. Response to Thermal Disturbance, J.*Phys. Soc. Jpn,* 12(1957), p. 570

[8] V. M. Agranovich, M. D. Galanin, Migration of Electron Energy Excitations in Condensed Matter, Nauka, Moskwa, 1978

[9] J. P. Šetrajčić, S. K. Jaćimovski, V. D. Sajfert, Phonon Engineering Theory of Crystalline Layered Nanostructures, p. 57, ISBN: 978-3659-80775-6, LAP Lambert Academ. Publ., Saarbrücken (Germany), 2015.

[10] J. P. Šetrajčić, S. K. Jaćimovski, S. M. Vučenović, Green's Functions in Quantum Statistical Physics – Condensed Matter Physics, International Conference on Applied Sciences, Banja Luka. 2022.

[11] A. Isihara, Statistical Physics, ISBN: 9781483274102, Academic Press, New York, 1971.

[12] S. V. Tyablikov, Methods of Quantum Theory in Magnetism, Nauka, Moscow. 1975.

[13] C. Kittel, Introduction to Solid State Physics, Wiley, New York, 1986.

[14] A. Jain, K. E. Goodson, Measurement of the Thermal Conductivity and Heat Capacity of Freestanding Shape Memory Thin Films Using the 3ω Method, *J.Heat Transfer*, r

[15] D. L. Nika, A. A. Balandin, Phonons and Thermal Transport in Graphene and Graphene-Based Materials, arXiv:1606.00488 [cond-mat. mtrl-sci], 56 pages, doi: https://doi.org/10.48550/arXiv.1606.00488; Rep Prog.Phys. 80, 036502, 2017.

[16] D. L. Nika, A. I. Cocemasov and A. A. Balandin, Specific heat of twisted bilayer graphene: Engineering phonons by atomic plane rotations, *Appl. Phys. Lett.*, 105(2014), 031904

[17] D. H. Santamore, M. C. Cross, The Effect of Surface Roughness on Universal Thermal Conductance, 1), *Phys.Rev.*B 63(2001); doi: 10.1103/PhysRevB.63.184306. 2) Physica B 316(1), 389-392 (2002); doi: 10.1016/S0921-4526(02)00522-7.

[18] Schwab et al, Measurement of the Quantum of Thermal Conductance, Nature 404, 974 (2000); doi: 10.1038/35010065.

[19] V. N. Popov, Low-Temperature Specific Heat of Nanotube Systems, *Phys.Rev.B*, 66(2002) 153408; doi: 10.1103/PhysRevB.66.153408

[20] A. Alofi, G. P. Srivastava, Phonon Conductivity in Graphene, *J.Appl.Phys.*, 112(2012), 013517; doi: 10.1063/1.4733690.

[21] A. I. Cocemasov, D. L. Nika, A. A. Balandin, Engineering of Thermodynamic Properties of Bilayer Graphene by Atomic Plane Rotations: the Role of out-of-plane Phonons, *Nanoscale*, 7(2015), 12851; doi: 10.1039/C5NR03579A.