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Diffraction from WS_2 and MoS_2 Nanotubes

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We present a symmetry based analysis of diffraction intensities of transition metal dichalcogenide nanotubes. Obtained results point out specific features of the intensity distribution that are related to group parameters. It is possible to read out all the group parameters from diffraction patterns, and therefore to characterize nanotube, since symmetry group uniquely determines the chiralty indices.

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1. Introduction

Following the discovery of carbon nanotubes, it was realized that this kind of perfectly organized nanostructures is not limited to carbon only. Soon, among other types of nanotubes, various inorganic nano- and microtubes were synthesized [1]. One of those were transition metal dichalcogenide tubular structures MS_2(M=Mo,W) which, unlike carbon tubes, are formed from more complex layered compounds. These structures have attracted much attention due to important applications as lubricants, electron devices, catalysts, super shock absorbers, etc.

Various techniques were successfully used for growing MS_2 tubules [1–3] with specific characteristics. The most common method for their characterization are X-ray and electron diffraction. Therefore, fast simulation and analysis of diffraction patterns is of great importance.

Here we use symmetry of MS_2 tubes to achieve this goal. Precisely, as symmetry of these compounds is described by line groups [4], we utilize recently developed symmetry based calculations of diffraction intensities[5, 6] for the line group orbits. In Sec. 3 we extract the relevant formulas and relationship between tube's group parameters and some characteristic features of diffraction patterns. In Sec. 4 we illustrate the method of tube's characterization from simulated diffraction patterns of MS_2 nanotubes.

2. Symmetry of MS_2 tubes

Any nanotube is a quasi one-dimensional system periodical along the tube axis (z-axis by convention). Therefore, its symmetry is described by one of the line groups. A single-wall MS_2 nanotube is three-layer sandwich: the middle layer is formed of metal atoms, while two other layers are from sulfur. Such tubes are building blocks for the multi-wall tubes.

As in the case of carbon nanotubes, structure of a single-wall MS_2 tubes is uniquely determined by its chiral indexes (n_1, n_2) (with integers $n_1 \geq n_2 \geq 0$). Depending on chirality, the symmetry group of nanotube belongs to one of three different families [7]:

$$\boldsymbol{L}_{\mathcal{C}} = \boldsymbol{T}^r_q(f)\boldsymbol{C}_n, \quad \boldsymbol{L}_{\mathcal{A}} = \boldsymbol{T}^1_{2n}(f)\boldsymbol{C}_{nh},$$
$$\boldsymbol{L}_{\mathcal{Z}} = \boldsymbol{T}^1_{2n}(f)\boldsymbol{C}_{nv} \tag{1a}$$

respectively for chiral, armchair and zig-zag tubes. Here group parameters are:

$$n = \mathrm{GCD}(n_1, n_2), \quad q = 2\frac{n_1^2 + n_1 n_2 + n_2^2}{q\mathcal{R}},$$
$$f = \sqrt{\frac{3n}{2\mathcal{R}q}}a_0, \tag{1b}$$
$$r = \frac{n_1 + 2n_2 - (\frac{n_2}{n})^{\mathrm{Eu}(\frac{n_1}{n})-1}q\mathcal{R}}{n_1\mathcal{R}} \bmod \frac{q}{n},$$
$$rp = n \pmod q, \tag{1c}$$

while $\mathrm{Eu}(x)$ is the Euler function, a_0 is lattice period of the corresponding 2D lattice, and $\mathcal{R} = 3$ if $(n_1 - n_2)/n$ is divisible by 3 and $\mathcal{R} = 1$ otherwise.

Regardless of chirality, single-wall MS_2 nanotube is a three orbit system: each S-M-S layer is generated by the action of the transformations from the group $\boldsymbol{T}^r_q(f)\boldsymbol{C}_n$ (for achiral tubes this is a halving subgroup of the symmetry group, while for the chiral ones it is complete group) on a single atom arbitrary chosen to represent the orbit. It is convenient to fix the coordinate system such that the orbit representative S_{in} (i.e. sulfur atom from the interior layer) is on the $x-$axis. Consequently, the cylindrical coordinates of the three orbit representatives are:

$$_{\mathrm{in}} = \left(\frac{D_{\mathrm{in}}}{2}, 0, 0\right), \quad r_{\mathrm{out}} = \left(\frac{D_{\mathrm{out}}}{2}, 0, 0\right),$$
$$r_{\mathrm{M}} = \left(\frac{D_{\mathrm{M}}}{2}, \phi_0, z_0\right) \tag{2}$$

with $\varphi_0 = 2\pi\frac{n_1+n_2}{nq\mathcal{R}}$ and $z_0 = \frac{n_1-n_2}{\sqrt{6}nq\mathcal{R}}a_0$, while $D_{\mathrm{in}}, D_{\mathrm{out}}$ and D_{M} are diameters of the interior sulfur, outer sulfur and M-layer respectively.

Symmetry groups of multi-wall tubes are easily found from Eq. (1a) if the walls' symmetry groups and their mutual position is known. Also, their number of orbits will

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be three times number of walls. For example, both compounds (MoS_2, WS_2) are known to crystalize in hexagonal 2Hb or rhombohedral 3R polytype. Tubes of such type have symmetry groups which are the same as their single-wall constituents [7].

3. Diffraction intensity

Within a framework of kinematical theory, the total diffraction intensity is an absolute square of the total scattering amplitude $F(k) = \sum_i f_i(k) \exp(2\pi \mathrm{i} k \cdot r_i)$ where $f_i(k)$ is the scattering amplitude of the i-th atom and $k = (k_{sc} - k_{\mathrm{in}})/2\pi$ (k_{sc} is scattered and k_{in} is the incident wave vector). It is easy to show that $F(k)$ is a sum over the orbits [6]:

$$F(\boldsymbol{k}) = \sum_A |\boldsymbol{Y}_A| F_A(\boldsymbol{k}). \tag{3}$$

Here A counts orbits, i.e. their initial (representative) atoms; the sum over atoms of the same orbit is

$$F_A(\boldsymbol{k}) = \frac{f_A(\boldsymbol{k})}{|\boldsymbol{Y}_A|} \sum_{y \in \boldsymbol{Y}_A} \mathrm{e}^{2\pi \mathrm{i} \boldsymbol{k} \cdot \boldsymbol{r}_{yA}} = f_A(\boldsymbol{k}) G^{\boldsymbol{Y}_A}(\boldsymbol{k}), \tag{4}$$

with $\boldsymbol{Y}_A$ and $\boldsymbol{r}_{yA}$ being the corresponding transversal (with $|\boldsymbol{Y}_A|$ elements) and the position of the atom obtained from the initial one by the transverzal element $y \in \boldsymbol{Y}_A$. While the term $G^{\boldsymbol{Y}_A}(\boldsymbol{k})$ is purely geometrical, the relevant physical information on the orbit is contained in the atom A diffraction power $f_A(\boldsymbol{k})$. All three orbits in a singe-wall MS_2 tube belong to the same confirmation class $\boldsymbol{Y}^{(1)}$. Their geometrical factors [6] are zero unless $k = k_K = (k_\perp, \Phi, K/a)$ ($K = 0, \pm 1, \ldots$):

$$G^{\boldsymbol{Y}_A}(\boldsymbol{k}) = \sum_M \mathrm{i}^{Mq-Kp} J_{Mq-Kp}(\pi D_A k_\perp) \times \mathrm{e}^{\mathrm{i}(Mq-Kp)(\Phi-\varphi_A)} \mathrm{e}^{\mathrm{i}2\pi z_A \frac{K}{a}}. \tag{5}$$

After substituting (2) in (3), the total scattering amplitude is:

$$\begin{aligned} F(\boldsymbol{k}_K) \propto{}& f_{\mathrm{Mo}}(k) \sum_M \mathrm{i}^{Mq-Kp} J_{Mq-Kp}(\pi D_{\mathrm{Mo}} k_\perp) \\ &\times \mathrm{e}^{\mathrm{i}(Mq-Kp)(\Phi-\varphi_0)} \mathrm{e}^{\mathrm{i}2\pi z_0 \frac{K}{a}} \\ &+ f_{\mathrm{S}}(k) \sum_M \mathrm{i}^{Mq-Kp} [J_{Mq-Kp}(\pi D_{\mathrm{in}} k_\perp) \\ &+ J_{Mq-Kp}(\pi D_{\mathrm{out}} k_\perp)] \, \mathrm{e}^{\mathrm{i}(Mq-Kp)\Phi} \end{aligned} \tag{6}$$

To conclude, diffraction intensity vanishes everywhere except within countable set of *layer lines* labeled by integer K, each of them is a plane perpendicular to the Z-axis at the height K/a). Note that only Bessel functions involve perpendicular distance $k_\perp$. As their order depends on the integer K, only the layer lines with zero order Bessel function are gapless, i.e. they have nonzero intensity at $k_\perp = 0$. Counter K of two adjacent gapless lines differs by q/n, i.e. there are $q/n - 1$ other layer lines. Among them, two for chiral and only one for achiral tubes have the minimal nonzero gap [6]: for these layer lines $K = \pm r + sq/n$ ($s = 0, \pm 1, \ldots$) and the minimal order of Bessel function in (6) is $\pm n$.

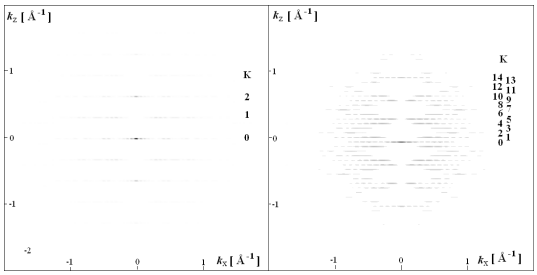

Fig. 1. Simulated X-ray diffraction patterns of MoS_2 tubes for normal incidence: left pattern is from tube (10,10), while the right one is from (6,3). Value of K for the first q/n layer lines is given. Region $k < 2$ Å^{-1} is presented.

4. Diffraction patterns

After we found intensity in terms of line group parameters, we want to single out those characteristic features of diffraction patterns (assuming normal incidence) sufficient to determine line group parameters. Firstly, the distance between two neighboring layer lines gives value of $1/a$. Secondly, the distance between the two neighboring gapless layer lines is $1/f$. As $f = an/q$, this gives integer q/n. Alternatively, simple counting of the lines above the equatorial line ($K = 0$) and finding K of the first gapless line gives q/n. Of course, this can be done only if we are sure that all in between lines are visible in the diffraction pattern. Parameter r (or $r' = q/n - r$) may be again found by counting, or once a is found it follows that $r = d_r/a$ where d_r is the distance of the first line with the narrowest gap. Finally, analysis of intensity oscillations along this layer line gives the remaining parameter n.

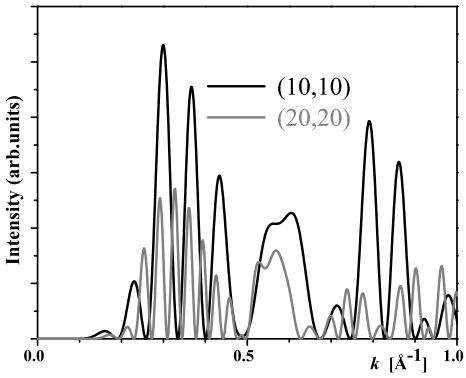

Fig. 2. Simulated diffraction intensity along the first layer line (with the narrowest gap) for the tubes (10,10) and (20,20) (diameters 1.04 nm and 1.91 nm.

To illustrate this, we have calculated X-ray diffraction intensity for $(10, 10)$ and $(6, 3)$ MoS_2 tubes. In Fig. 1 normal incidence diffraction patterns are given. From the left pattern it is obvious that it comes from an achiral tube as there is always just one line between the two

gapless layer lines. Thus $q/n = 2$ and $r = 1$. After calculating the period a, it becomes clear that this is an armchair tube. Finally, in order to determine the tube chiral indices, n has to be found by fitting the intensity along first layer line which is plotted in Fig. 2. In similar fashion, from the right pattern in Fig. 1, it follows that $q/n = 14$ and $r = 5$ or $r' = 9$. There are two possible helical parameters r as they correspond to optical isomers, which are not distinguishable by diffraction only. There is no need to calculate a for chiral tubes, as their structure is uniquely determined by three group parameters q, r and n. Remaining parameter n is found by fitting the intensity along layer line with $K = r$. It is worth noticing that intensity oscillations along the equatorial line reveal information about the tube diameter D_{out}: as the diameter of each layer is parameter of the Bessel function $J_0(\pi D k_\perp)$, obviously the first local minimum of $I(\boldsymbol{k}_0)$ is due to the Bessel function of the outer sulfur. More detailed analysis may give information abut the interlayer distance of single-wall MoS_2.

5. Conclusions

Using symmetry based classification of the quasi one-dimensional elementary systems, we derived an expressions for diffraction intensity of singe-wall MS_2. Additionally, diffraction pattern analysis revealed characteristic features related to particular symmetries. This enables to determine chiral indices for arbitrary singe-wall MS_2 tube. Obtained results can be further used to calculate and analyze diffraction patterns of various type of multi-wall tubes.

Acknowledgements

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