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*Division A – Division for
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Formation of a chemical compound layer due to reaction diffusion process.

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Abstract. A model is developed that described the growth kinetics of a compound layer during a reaction-diffusion process. The compound layer formation occurs at the interfaces of two insoluble solid layers. The compound layer is formed as a result of chemical reaction between the diffusing species and surface atoms. The layer growth occurs in two stages; the first growth stage is controlled by chemical reaction while the second growth stage is controlled by diffusion. A critical thickness and time are obtained at the transition point between the two growth stages. The result of this model shows a layer growth kinetics that is complex than linear and parabolic laws. The complexity of the growth kinetics is ascribed to the simultaneous diffusion of two kinds of atomic species in the compound layer.

1. Introduction

A compound layer is formed as a result of reaction-diffusion process at the interfaces of two insoluble layers [1-2]. This phenomenon has been confirmed experimentally for different substances within a certain range of formation temperature [3-13]. The growth kinetics of a compound layer can be described by linear-parabolic growth law [14]. As a rule, the parabolic law describes diffusion limited growth while reaction controlled growth is delineated by linear law especially at the beginning of the reactive diffusion process. Failure to acknowledge the importance of chemical reaction in compound layer formation process results in loss of reaction controlled growth [15]. Unfortunately, most of the experimental works considered only diffusion limited growth.

The rate of chemical reaction is one of the most important factors, which determines the growth of a compound layer. The reactant species concentration dependence on chemical reaction rate is complex. The explicit dependence and its theoretical justification are established only for the simplest systems. For example, the reaction rate of a mixture of ideal gases can be described as the product of their concentrations because reaction rate is proportional to the probability of collision between the reacting gas atoms. If one of the reactants is taking in excess such that its concentration remains practically invariant during the reaction, the rate of reaction become independent of the concentration of this reactant [16]. Such behaviour is typical for the solid state reactions where the number of possible neighbouring sites for each atom is strictly limited, and the reaction occurs only between the nearest neighbours. For instance, if all possible sites around *B* atoms are occupied by *A* atoms in a particular *AB* compound layer configuration, further increasing of concentration of *A* atoms would have no effect on reaction rate. Thus, the reaction rate becomes sensitive to the deviation from stoichiometry and remains invariant when the concentration changes within a wide range. However, such behaviour makes it possible to build a simple approximation of the reaction rate as a function of concentration.

In this study, we present a model that is developed on a simple approximation of reaction rate as a function of reactant species densities. This model takes into consideration the contribution of chemical reaction to the compound layer formation during both reaction controlled and diffusion limited growth stages. The result that follows from this consideration provides new insight on the growth kinetics of a compound layer in solid state reaction.

2. Model and basic equation

The chemical reaction between A and B atoms, is represented as thus:



Where ν_a and ν_b are stoichiometric coefficients of A and B atoms respectively.

At the initial time $t = 0$, the thickness $h(t)$ of AB compound layer is equal to zero.

Suppose that the reaction in (1) occurs only at the interfaces and not inside the A and B layers.

Due to diffusion, A atoms traverse from A layer through the AB layer toward interface AB/B , where they react with B atoms to form AB compound. B atoms likewise diffuse in opposite direction, from B layer through the AB layer toward interface A/AB . This interaction gives rise to additional AB compound. $h(t) = h_a(t) + h_b(t)$, where $h_a(t)$ and $h_b(t)$ are the thicknesses of AB compound layer which formed as a result of chemical reaction between A and B atoms at interfaces A/AB and AB/B respectively.

The rate of chemical reaction ϕ at interfaces of solid layers depends on densities of A and B atoms in a complex manner. However if there exist excess of A (or B) atoms, then the rate of reaction remain invariant with a change of density of A (or B) atoms [16]. On the other hand, if densities of A and B atoms are approximately equal ($\nu_a n_a \approx \nu_b n_b$), then rate of AB compound formation can be represented in the first approximation as product of A and B atom densities

$$\phi = \beta n_a n_b \quad (2)$$

ϕ is the symmetric function on both densities. n_a and n_b are the densities of A and B atoms which move to AB/B interface (at $x = h_b(t)$) and A/AB interface (at $x = -h_a(t)$) respectively and β is the reaction rate constant.

Assuming that A atoms are in excess at AB/B interface ($\nu_a n_a(h_b(t)) > \nu_b n_b^0$). Taking into account that density of B atoms at interface AB/B is constant ($n_b(h_b(t)) = n_b^0$), in this case, we can approximate rate of reaction at interfaces AB/B and A/AB as thus:

$$\phi(h_b(t)) = \begin{cases} \beta (n_b^0)^2 = \text{const} & \nu_a n_a \geq \nu_b n_b^0 \\ \beta n_b^0 n_a(h_b(t)) & \nu_a n_a \leq \nu_b n_b^0 \end{cases} \quad \text{and} \quad \phi(-h_a(t)) = \begin{cases} \beta n_a^0 n_b(-h_a(t)) & \nu_a n_a^0 > \nu_b n_b \\ \beta n_a^0 n_b^0 = \text{const} & \nu_a n_a^0 \leq \nu_b n_b \end{cases} \quad (3)$$

n_a^0 and n_b^0 are densities of A and B surface atoms in A and B layers respectively.

Densities of A and B atoms change inside the AB compound layer as the formation process progresses.

Density of A atoms decrease from n_a^0 (at $x = -h_a(t)$) to $n_a(h_b(t))$, and that of B atoms decrease from n_b^0 (at $x = h_b(t)$) to $n_b(-h_a(t))$.

At certain moment of time, t_c ,

$$\nu_a n_a(t_c) = \nu_b n_b^0 \quad (4)$$

Let t_c denotes the critical time. At $t < t_c$, the number of A atoms at interface AB/B is more than B atoms, and the growth of the AB compound layer is controlled by chemical reaction. Reaction rate at AB/B interface is $\phi = \beta n_b^0 n_b^0$ and at A/AB interface $\phi = \beta n_a^0 n_b(-h_a(t))$. At $t > t_c$, the AB layer growth is controlled by diffusion and reaction rate is $\phi = \beta n_b^0 n_a(h_b(t))$ at AB/B interface and

$\phi = \beta n_a^0 n_b(-h_a(t))$ at A/AB interface.

The growth rate of AB layer is, therefore, described in terms of reaction rate as follows:

$$\frac{dh(t)}{dt} = \frac{dh_a(t)}{dt} + \frac{dh_b(t)}{dt} = V_{ab}(\phi(-h_a(t)) + \phi(h_b(t))) \quad (5)$$

Where V_{ab} is the volume per molecule of the AB compound layer.

Suppose all A atoms at AB/B interface and all B atoms at A/AB interface react at once. Therefore the growth of AB compound layer is determined by the flux of A atoms, J_a toward AB/B interface and flux of B atoms, J_b toward A/AB interface.

Thus, we consider diffusion of A atoms and B atoms inside the AB compound layer.

Diffusion of A and B atoms inside the AB layer is described by Fick's second law under a stationary condition as:

$$D_a \frac{\partial^2 n_a(x)}{\partial x^2} = 0 \text{ and } D_b \frac{\partial^2 n_b(x)}{\partial x^2} = 0 \quad (6)$$

and the boundary conditions are:

$$n_a(-h_a(t)) = n_a^0, J_a(h_b(t)) = -D_a \nabla n_a(x=h_b(t)) = v_a \phi(h_b(t)), n_b(h_b(t)) = n_b^0, \text{ and } J_b(-h_a(t)) = -D_b \nabla n_b(x=-h_a(t)) = v_b \phi(-h_a(t))$$

Diffusion coefficients of A and B atoms are D_a and D_b respectively. Solving (6) for the first growth stage (when $t < t_c$), we obtain a general expression for the distribution of A and B atoms inside the AB compound layer as:

$$n_a(x, t) = -\frac{\beta(n_b^0)^2 v_a}{D_a} (x + h_a(t)) + n_a^0 \text{ and } n_b(x, t) = \frac{\beta n_a^0 n_b^0 v_b}{D_b + \beta n_a^0 v_b h(t)} (x - h_b(t)) + n_b^0 \quad (7)$$

According to (7), densities of A atoms at $h_b(t)$ and B atoms at $x = -h_a(t)$ are:

$$n_a(h_b(t)) = \frac{D_a n_a^0 - \beta(n_b^0)^2 v_a h(t)}{D_a} \text{ and } n_b(-h_a(t)) = \frac{D_b n_b^0}{D_b + \beta n_a^0 v_b h(t)} \quad (8)$$

Equation (8) gives the number of A and B atoms that diffuse to reaction interfaces AB/B and A/AB respectively.

The growth rates at A/AB and AB/B interfaces at $t < t_c$ are described by:

$$\frac{dh_a(t)}{dt} = \beta n_a^0 n_b(-h_a(t)) V_{ab} \text{ and } \frac{dh_b(t)}{dt} = \beta(n_b^0)^2 V_{ab} \quad (9)$$

Substituting (8) & (9) into (5), we obtain closure for $h(t)$ and solving it leads to an expression connecting time and thickness of AB compound layer together at $t < t_c$

$$t = \frac{v_a h(t)}{\beta v_b V_{ab} (n_b^0)^2} - \frac{D_b v_a^2}{\beta^2 v_b^3 V_{ab} (n_b^0)^3} \ln \left[\frac{\beta n_a^0 n_b^0 v_b^2 h(t)}{D_b (n_a^0 v_a + n_b^0 v_b)} + 1 \right] \quad (10)$$

This equation depicts a partly linear and partly natural logarithm dependence of time on layer thickness. The presence of natural logarithm in this growth kinetics is ascribed to simultaneous diffusion of A and B atoms inside the AB layer.

Substituting the density of A atoms in (8) into (4), we obtain thickness of AB compound layer at critical time as:

$$h_c = \frac{D_a(n_a^0 v_a - n_b^0 v_b)}{\beta v_a v_b (n_b^0)^2} \quad (11)$$

h_c is the critical thickness of AB layer at the transition point. The transition takes place at AB/B interface and, the diffusing atom at this interface is A-atom; therefore, the critical thickness depends on the diffusivity of A atoms.

For critical time $t = t_c$, $h(t = t_c) = h_c$; inserting (11) into (10) we obtain

$$t_c = \frac{D_a(n_a^0 v_a - n_b^0 v_b)}{\beta^2 v_b^2 V_{ab} (n_b^0)^4} \left[1 - \frac{D_b v_a^2}{\beta v_b^2 D_a n_b^0 V_{ab} (n_a^0 v_a - n_b^0 v_b)} \ln \left(1 + \frac{D_a n_a^0 (n_a^0 v_a - n_b^0 v_b)}{v_a D_b n_b^0 (n_a^0 v_a + n_b^0 v_b)} \right) \right] \quad (12)$$

The critical time is shown as a non-linear function of diffusion coefficients of A and B atoms in (12).

For second growth stage ($t > t_c$), the growth of the AB compound layer is diffusion limited at both interfaces. Expressions for dh_a/dt and the density of B atoms at $x = -h_a(t)$ remain the same because the layer growth kinetics at A/AB interface is invariant (i.e. always diffusion limited). Expression for density of A atoms at $x = h_b(t)$ change due to transition of layer growth process from reaction controlled process to diffusion limited process:

$$n_a(h_b(t)) = \frac{D_a n_a^0}{D_a + \beta n_b^0 v_a (h_a(t) + h_b(t))} \quad (13)$$

and for the growth rate of AB compound layer as a result of chemical reaction at interface AB/B, we have:

$$\frac{dh_b(t)}{dt} = \beta n_b^0 n_a(h_b(t)) V_{ab} \quad (14)$$

Hence, the growth rate of AB compound layer at second growth stage at time $t > t_c$ becomes:

$$\frac{dh(t)}{dt} = \beta n_a^0 n_b(-h_a(t)) V_{ab} + \beta n_b^0 n_a(h_b(t)) V_{ab} \quad (15)$$

Solving (15), we obtain a relationship between time and thickness of AB compound layer:

$$t - t_c = \alpha(h^2(t) - h_c^2) + \lambda(h(t) - h_c) - \sigma \ln \left[\frac{\xi h(t) + \psi}{\xi h_c + \psi} \right] \quad (16)$$

Where

$$\alpha = \frac{1}{2V_{ab} [D_b n_b^0 + D_a n_a^0]}, \xi = \beta [D_b n_b^0 + D_a n_a^0], \psi = D_a D_b$$

$$\lambda = \frac{[(D_a n_a^0)^2 + (D_b n_b^0)^2]}{\beta V_{ab} n_a^0 n_b^0 [D_b n_b^0 + D_a n_a^0]^2}, \sigma = \frac{D_a D_b [D_a n_a^0 - D_b n_b^0]^2}{\beta^2 V_{ab} n_a^0 n_b^0 [D_b n_b^0 + D_a n_a^0]^3}$$

Equation (16) shows a partly parabolic and partly natural logarithm dependence of time on layer thickness which is also due to simultaneous diffusion of A and B atoms inside the AB layer.

3. Result and discussion

The growth of AB compound layer described in the model is determined by the rate of chemical

reaction at both interfaces during reaction controlled and diffusion-limited process. The natural logarithm dependence of time on layer thickness shown in (10) and (12) arises from the diffusion of two kinds of atomic species by means of two different transport mechanisms taking place at the same time in the AB compound layer. A linear dependence of time on layer thickness can be obtained in (10) if only one kind of atomic species diffuses in the growing AB layer (for example, when $D_b = 0$). The same approach can be employed in (12) if $D_b = 0$, a parabolic dependence of time on layer thickness is obtained. In other words, if only one kind of atomic species diffuses at a time, a linear growth would occur during the reaction controlled process and parabolic during diffusion limited process. Thus a linear-parabolic growth is possible in this situation only if there is an excess of A atoms at the reaction interface at the beginning of the formation process.

Another situation that may arise when only one kind of atomic species diffuse in the AB compound layer is when there is a small number of diffusing atoms at the reaction interface at the beginning of the reactive diffusion process. The rate of chemical reaction would depend on densities of both diffusing species and surface atoms which would result in a parabolic growth. Therefore, only one stage of growth would be feasible and, this growth would take place during diffusion limited process.

The critical thickness of nickel silicide, Ni_2Si estimated from this model based on the result presented here, is in close agreement with the experimental work in [3]. The estimated critical thickness of Ni_2Si is 3.8 nm which is close to 3.3 nm measured from experimental work. Figure 1 shows a linear-parabolic growth during the formation of nickel silicide at temperature $260\text{ }^\circ\text{C}$. Nickel is the only active diffusing species in the nickel silicide layer, and the density of nickel is more than that of silicon at the beginning of the chemical reaction since Ni_2Si phase is rich in nickel.

On palladium silicide, Pd_2Si the estimated critical thickness is 2.1 nm , but we do not have any experimental result to compare with this value because no experiment is done yet on the critical thickness of Pd_2Si .

There are different viewpoints on the diffusing species in the palladium silicide layer from experimental reports [2]. We, therefore, investigate the diffusing species in the growing palladium silicide layer looking at three diffusion possibilities when: 1) only silicon diffuses, 2) only palladium diffuses, and 3) both silicon and palladium diffuse concurrently. We then estimate the thickness of palladium silicide under each diffusion possibility and compared it with experimental result in [4]. The result shows that silicon is the best candidate for this case because the curve of palladium silicide layer under the diffusion of silicon is closer to the experimental curve than the other two curves. This is depicted in figure 2.

The result also shows that the concurrent diffusion of palladium and silicon species in the growing Pd_2Si layer is not feasible since the thickness of silicide estimated under this condition is more than that of experimental value; but we cannot rule out the possibility of palladium participation in the diffusion process during the silicide growth, and this can possibly occur, if only if the diffusion of silicon is obstructed [6].

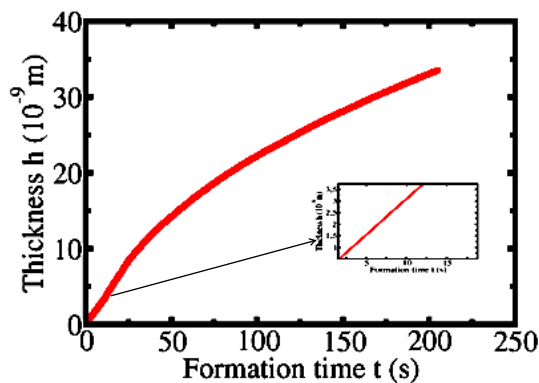


Figure 1. The linear-parabolic growth kinetics of nickel silicide, Ni_2Si at temperature 260°C . The arrow shows the linear growth regime of Ni_2Si

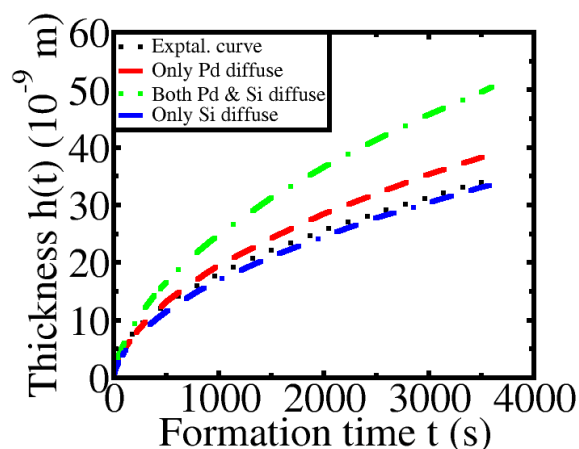


Figure 2. The growth kinetics of palladium silicide, Pd_2Si at 200°C under the consideration of three different diffusion possibilities over a period of 3600 s.

4. Conclusion

This study shows that dependence of time on layer thickness is complex than linear, and parabolic law as the number of kinds of diffusing species exceed one in the growing AB compound layer. A linear-parabolic and parabolic layer growth kinetics are feasible if only one kind of atomic species diffuses inside the AB compound layer at a time.

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Influence of alkaline earth metal cations; Ca^{2+} , Sr^{2+} and Ba^{2+} on the structural and optical properties of MAl_2O_4 : Eu^{2+} , Nd^{3+} phosphors

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Abstract. Eu^{2+} doped and Nd^{3+} co-doped MAl_2O_4 : Eu^{2+} , Nd^{3+} ($\text{M} = \text{Ca}$, Sr , and Ba) phosphors were prepared by a solution-combustion method. The obtained powders were investigated in terms of their phase composition, particle morphology and photoluminescence (PL) by X-Ray diffraction (XRD), Scanning Electron Microscope (SEM) and Ultraviolet-Visible Spectroscopy (UV-VIS) techniques respectively. XRD analysis depicts a monoclinic phase for CaAl_2O_4 : Eu^{2+} , Nd^{3+} and SrAl_2O_4 : Eu^{2+} , Nd^{3+} and a hexagonal structure for BaAl_2O_4 : Eu^{2+} , Nd^{3+} phosphor. SEM results showed generally agglomerated particles with non-uniform shapes and sizes with irregular network structures having lots of voids and pores. PL excitation revealed broadband spectra with peaks corresponding to the crystal field splitting of the Eu^{2+} d-orbital. The emission spectra were also broadband with peaks at 447 nm for CaAl_2O_4 : Eu^{2+} , Nd^{3+} , at 507 nm for SrAl_2O_4 : Eu^{2+} , Nd^{3+} and at 497 nm for BaAl_2O_4 : Eu^{2+} , Nd^{3+} due to the $4f^65d^1-4f^7$ emission of Eu^{2+} . Sharp emission lines were observed arising from the f-f transitions of the Eu^{3+} ions. The differences in emissions from the three phosphors arise from the crystal field splitting of the 5d electron shell due to the changes in the crystalline environment of the Eu^{2+} ions caused by the substitution of the divalent alkaline earth metal cations with different ionic sizes in the MAl_2O_4 host lattice. UV-VIS spectra showed absorption edges at 330, 342 and 340 nm in agreement with the observed PL excitation peaks. The luminescence decay characteristics showed that BaAl_2O_4 : Eu^{2+} ; Nd^{3+} gave a longer afterglow as compared to the other two phosphors.

Keywords: CaAl_2O_4 : Eu^{2+} ; Nd^{3+} , SrAl_2O_4 : Eu^{2+} ; Nd^{3+} , BaAl_2O_4 : Eu^{2+} ; Nd^{3+} , Substitution, Crystal field, Luminescence, Transition, Long afterglow.

1. Introduction

The luminescent properties of divalent europium ion (Eu^{2+}) doped alkaline earth aluminates MAl_2O_4 : Eu^{2+} ($\text{M} = \text{Ca}$, Ba , Sr) have been widely studied owing to their high quantum efficiency in the visible region [1]. As compared with traditional sulfide based phosphors Eu^{2+} doped aluminate (Al_2O_3) phosphors have shown excellent photo-resistant, high chemical stability, endurance in storage, radiation resistance and can withstand different environmental conditions [2]. In these phosphors, the emission emanates from the $4f^65d^1 - 4f^7$ transition of Eu^{2+} . Depending on the host structure this emission can be

colour-tuned from ultraviolet to the red since the excited $4f^65d^1$ configurations of Eu^{2+} ion is highly sensitive to the change in the lattice environment [1,3].

SrAl_2O_4 belongs to distorted stuffed tridymite type structure. There are two, nine coordinated, crystallographic sites for Sr^{2+} . The two sites are said to only differ by a slight distortion of their square planes [4]. The Sr^{2+} and Eu^{2+} ions are very similar in their ionic size (i.e. 1.21 and 1.20 Å respectively). This means that Eu^{2+} occupy Sr^{2+} positions in the crystal structure. In a given host, the emission of Eu^{2+} is influenced by covalency, size of the cation, strength of the crystal field as well as alignment. On alignment, it is reported that, in BaAl_2O_4 and SrAl_2O_4 , the Sr and Ba ions form linear chains in the lattice [5].

Several methods have been used to synthesis Al_2O_4 phosphors such as solid state reaction [1] and sol-gel [4] among others. The synthesis of phosphors in this study has been achieved via a solution combustion route where the starting materials were mixed in solution phase. This process is very facile, safe, energy and time saving [6]. The method makes use of the heat energy liberated by the redox exothermic reaction between metal nitrates and urea as fuel [7]. In this study the effect of different alkaline earth metal cations; Ca^{2+} , Sr^{2+} and Ba^{2+} on the structural and optical properties of $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}$ (M = Ca, Ba, Sr) phosphors were investigated.

2. Experimental

The polycrystalline Eu^{2+} doped and Nd^{3+} co-doped $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}$ (M = Ca, Ba, Sr) phosphors were prepared by a low temperature urea–nitrate solution combustion reaction between stoichiometric mixtures of $\text{Ba}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3$, $\text{Nd}(\text{NO}_3)_3$, urea $\text{CO}(\text{NH}_2)_2$ as a fuel and boric acid (H_3BO_3) as a flux. The masses were weighed and mixed in 10ml of de-ionized water and stirred for 15 minutes at room temperature on a magnetic stirrer. The solutions were then poured into China crucibles and placed one at a time in a muffle furnace pre-heated at 500 °C. Exothermic reaction occurred, producing white, voluminous foam-like ash which was then milled to obtain the phosphor powders.

The structure and phase purity of the phosphor samples was checked with a Bruker-AXS D8 Advance X-ray diffractometer operating at 40 kV and 40 mA using $\text{Cu K}\alpha = 0.15406$ nm. The morphologies of the phosphor powders were obtained by using a Shimadzu Super scan SSX-550 scanning electron microscope (SEM). Absorption spectra were recorded using a Perkin Elmer Scan-Lambda 950 UV-Vis spectrophotometer. The PL excitation, emission and decay spectra were measured using a Cary Eclipse luminescence spectrometer (model LS-55) with a built-in 150 W xenon flash lamp as the excitation source and a grating to select a suitable excitation wavelength. In each case, equal quantities of the samples were excited with a beam having the same intensity directed on the same surface area.

3. Results and discussions

3.1. Structure (XRD)

XRD patterns of the $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}$ (M = Ca, Ba, Sr) phosphor powders are shown in fig. 1(a)-(d). The peaks indexed well with the JCPDS card numbers 71-1323, 70-0134 and 74-0794 for the BaAl_2O_4 , CaAl_2O_4 and SrAl_2O_4 respectively [3,8,9]. These compounds have a stuffed tridymite structure with a 3D frame work of corner sharing AlO_4 tetrahedra in which charge balance is achieved by the divalent cations that occupy interstitial sites [10]. At room temperature, BaAl_2O_4 is hexagonal with space group P6_3 having unit cell parameters 2a, c [11]. There are two different barium (Ba^{2+}) sites, one occurring 3 times more frequently than the other. Both Ba^{2+} sites are coordinated by 9 oxygen ions (O^{2-}). The channels are along the c-axis and the two different Ba^{2+} sites occur in separate chains [12]. SrAl_2O_4 belongs to the monoclinic P2_1 space group at room temperature [13].

The strontium (Sr) chains are along the a-axis [1]. There are two sites available for Sr^{2+} ions. Both sites occur in equal amounts in the lattice and are coordinated by 9 O^{2-} ions. The coordination of Sr by O_2 is less regular than the coordination of Ba by O_2 in BaAl_2O_4 [11]. CaAl_2O_4 has a monoclinic structure with space group $\text{P2}_{1/n}$ and three different sites for the Ca^{2+} ion one having 9-fold coordination and others

are 6-fold coordinated with O_2 atoms [14]. Since the samples were as-prepared and not annealed, unlabelled peaks in angle range of 30-35deg 2theta could be attributed to impurity phases due to unreacted precursors [15]. Majority of these peaks are also not reflected in the respective JCPDS card numbers. It was also reported that, the presence of other phases or some of the precursors can be attributed to the fact that the combustion wave is not uniform and a portion of the precursors might not react completely during the combustion process [16].

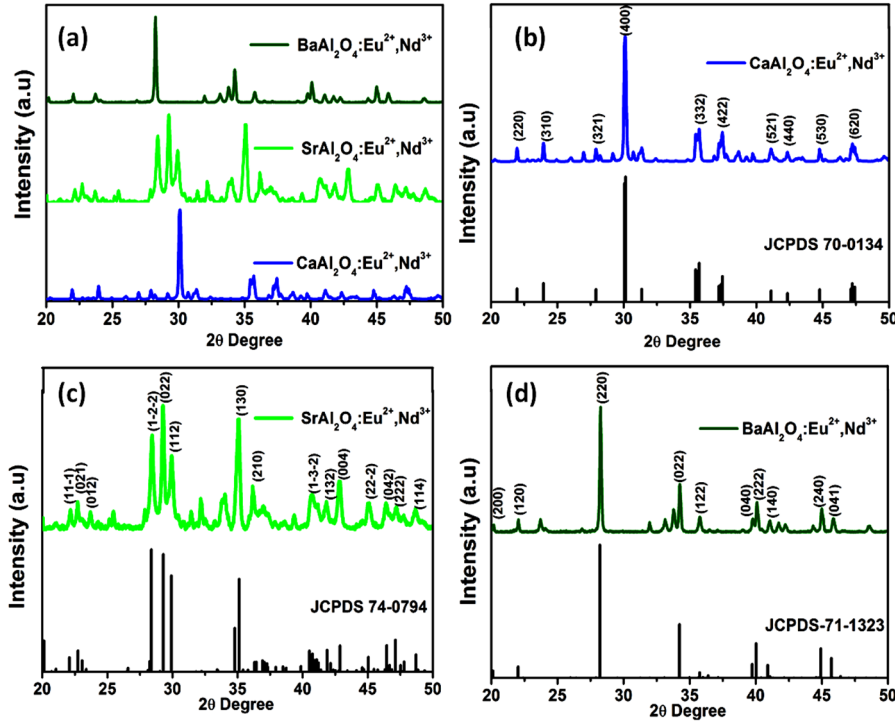


Fig. 1. (a)-(d): XRD patterns of $BaAl_2O_4:Eu^{2+};Nd^{3+}$, $CaAl_2O_4:Eu^{2+};Nd^{3+}$ and $SrAl_2O_4:Eu^{2+};Nd^{3+}$ phosphor powders.

3.2. Morphology(SEM)

Fig. 2(a), (b) and (c) show SEM micrographs for as – prepared $MA_2O_4:Eu^{2+}$ ($M = Ca, Ba, Sr$) phosphors. From fig. 2(a) and (b) it can be observed that powders are in the form of agglomerates with non-uniform shapes and sizes caused by non-uniform distribution of temperature and irregular mass flow during combustion [15]. In all these images, the surfaces of the particles contained fine pores and voids or cracks, which may be attributed to the evolved gases during combustion [16].

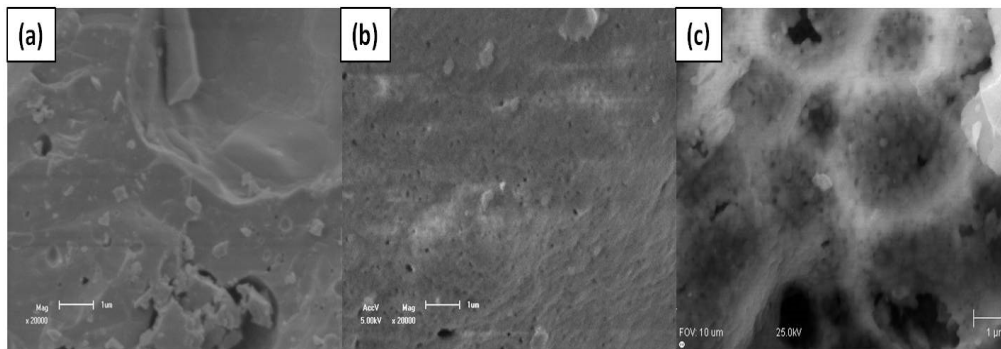


Fig. 2: (a), (b) and (c); SEM micrographs as – prepared $CaAl_2O_4:Eu^{2+};Nd^{3+}$, $SrAl_2O_4:Eu^{2+};Nd^{3+}$ and $BaAl_2O_4:Eu^{2+};Nd^{3+}$ phosphors respectively.

3.3. Photoluminescence (PL)

Fig. 3(a) and (b) show the PL excitation and emission measurements from $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$) phosphors. Excitation spectra were broadband revealing peaks arising from the Eu^{2+} d-orbital which is positioned in the band gap as a result of crystal field splitting [17,18]. These phosphors are wide band gap materials; SrAl_2O_4 (6.52 eV) [8], BaAl_2O_4 (6.5 eV) [19] and CaAl_2O_4 (5.78 eV) [20] so that no transition between the valence band (VB) and conduction band (CB) can occur under UV irradiation or the light with wavelengths ranging from 280 to 480 nm cannot excite the electrons from the VB to the CB it is the electrons of emission centre (Eu^{2+}) that is excited but not that of the host crystal [21,22]. The emission spectra were also broadband with peaks at 447 nm for $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$, at 507 nm for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ and at 497 nm for $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ due to the $4f^65d^1-4f^7$ emission of Eu^{2+} . Sharp emission lines were observed at 612 and 652 nm for $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$, at 615 nm for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ and at 610 nm for $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ arising from the f-f transitions of the Eu^{3+} ions. This could be attributed to the presence of residual unreduced Eu^{3+} ions resulting in simultaneous emissions from Eu^{2+} and Eu^{3+} [23].

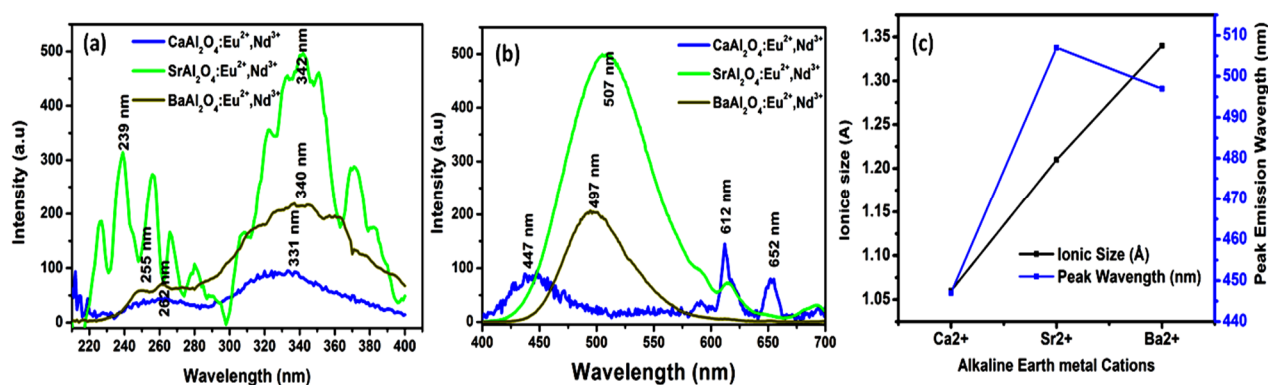


Fig. 3 (a) Excitation, (b) emission spectra of $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$) phosphor powders respectively and (c) emission peak as a function of different ionic sizes.

Differences in emission peaks maxima from the phosphors were observed as presented in fig. 3(c). They arise from the crystal field splitting of the 5d electron shell due to the changes in the crystalline environment of the Eu^{2+} ions caused by the substitution of the divalent alkaline earth metal cations with different ionic sizes Ca^{2+} (1.06Å), Sr^{2+} (1.21Å) and Ba^{2+} (1.34Å), in the MAl_2O_4 host lattice resulting a small shift of the emission maxima from 445 nm to 507 nm. It was reported that substitution of Sr^{2+} ions by smaller Ca^{2+} ions in the SrAl_2O_4 lattice increases the covalency of Eu-O bond [24]. This led to decrease in the energy splitting between the 5d levels of Eu^{2+} ions. On the other hand substitution of Sr^{2+} by Ba^{2+} ions reduces the covalency and the $4f^65d^1$ band is shifted to the lower energy side that led to the red shift in the emission maximum [24]. It was also observed that $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ had highest intensity followed by $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ phosphors and $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ in that order.

The fitted PL decay curves for the $\text{MAl}_2\text{O}_4:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$) phosphors are presented in fig. 4(a)-(d). In this study $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ gave a longer afterglow as compared to the other two phosphors [25]. The luminescent decay time for the transitions between the 4f–5d transition of Eu^{2+} ions levels is typically in the range of μs to ms which could be attributed to energy transfer process between traps and emission states resulting from Eu^{2+} and Nd^{3+} doping [18]. Although the decay process of luminescence is very complicated, it is certain that long decay times can be attributed to traps with different depths [18].

The Commission International de l'Eclairage (CIE) chromaticity co-ordinates of PL spectra and the UV-VIS reflectance profiles of all the samples are shown in fig. 4 and 5 respectively. From fig. 4, it was observed that the CIE coordinates effectively represent the emission wavelength of each phosphor as confirmed by the PL emission spectra. Substitution of part or whole of Sr sites by Ca or Ba ions can

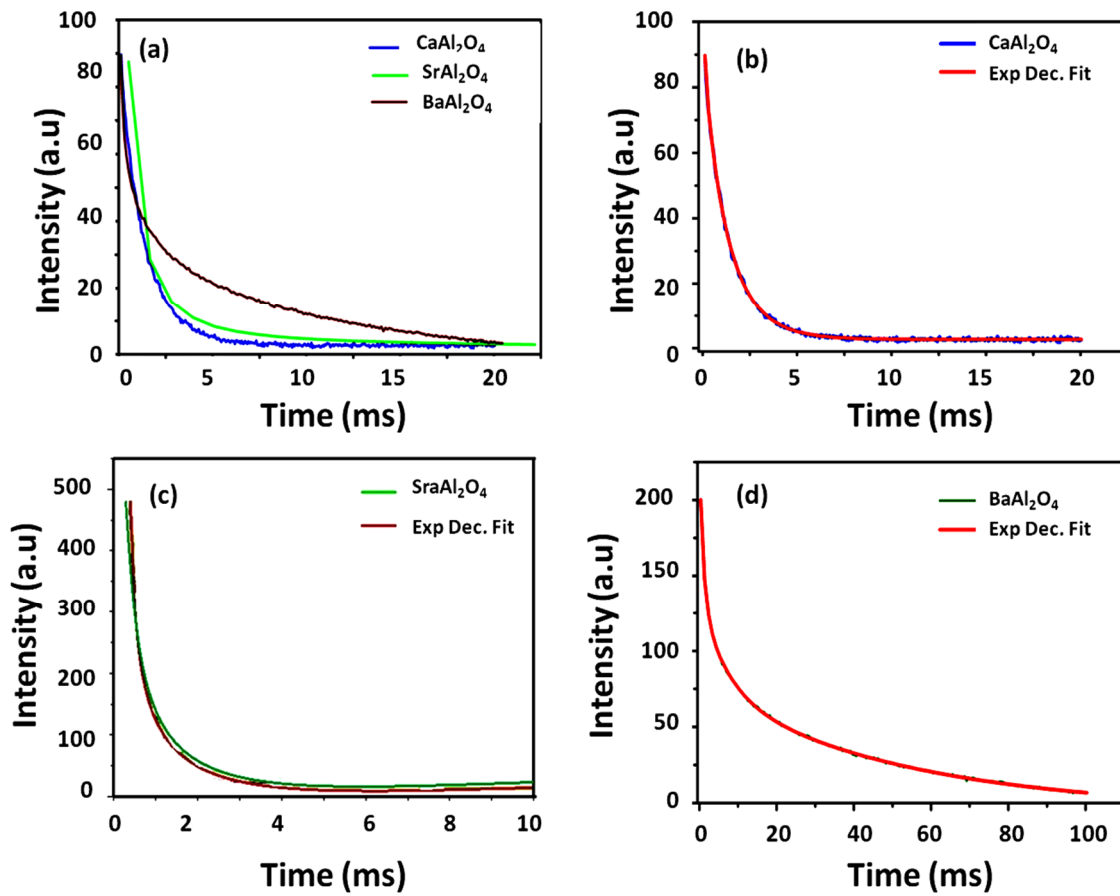


Fig. 4 (a) - (d). Experimental afterglow decay curves of $\text{MAL}_2\text{O}_4:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$) phosphors respectively.

effectively monitor the color of emission light and hence its CIE values. When Sr was substituted by Ca, bluish-white luminescence was observed [24]. Fig. 5 shows how absorption/reflectance is influenced by substitution of Ca^{2+} , Sr^{2+} and Ba^{2+} with different ionic sizes in the MAL_2O_4 host structure. The absorption bands of the colour centers were found to be broad and peaked approximately at 330, 342 and 340 nm in the range between 200 nm and 800 nm corresponding with the PL excitation wavelengths of each sample as shown in fig. 3(a). The peaks in the red region; 565 -760 represent f-f transition due to the possible presence of the unreduced Eu^{3+} ions [23].

4. Conclusion

In this study $\text{CaAl}_2\text{O}_4:\text{Eu}^{2+}; \text{Nd}^{3+}$, $\text{BaAl}_2\text{O}_4:\text{Eu}^{2+}; \text{Nd}^{3+}$ and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}; \text{Nd}^{3+}$ phosphors were prepared using the solution-combustion technique. The effect of varied the effect of different alkaline earth metal cations; Ca^{2+} , Sr^{2+} and Ba^{2+} on the structural and optical properties of $\text{MAL}_2\text{O}_4:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Ba}, \text{Sr}$) phosphors were investigated. It was found that the PL excitation and emission were greatly influenced by the substitution of the metal cations in the host structure which caused peak shifts. This was attributed to the different ionic sizes of these metal cations causing lattice distortions of the host matrix and hence affecting the crystal field around the luminescent centre. Sharp emission lines were observed arising from the f-f transitions of the Eu^{3+} ions.

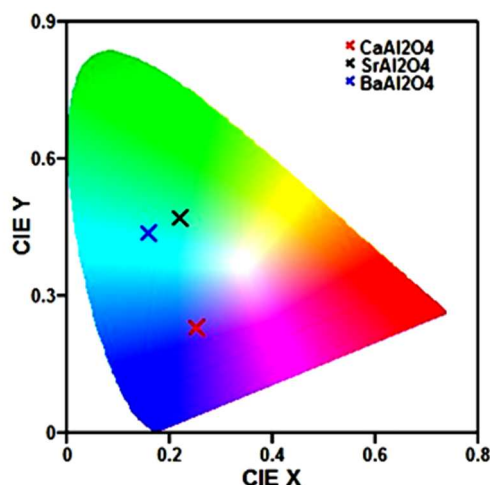


Fig. 4: (CIE) chromaticity co-ordinates for $\text{MAL}_2\text{O}_4:\text{Eu}^{2+}$ (M = Ca, Ba, Sr) phosphors.

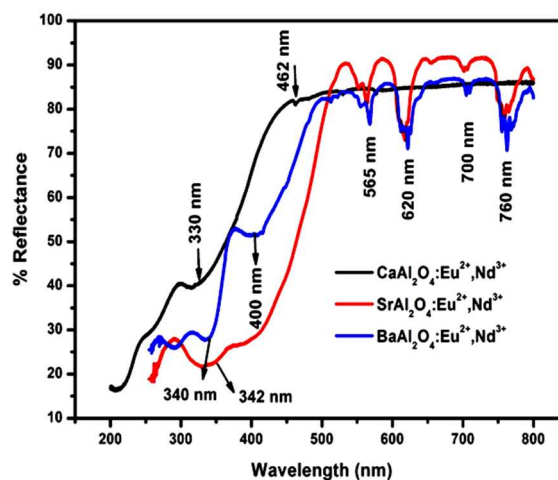


Fig. 5: UV-VIS reflectance spectra for $\text{MAL}_2\text{O}_4:\text{Eu}^{2+}$ (M = Ca, Ba, Sr).

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Division B – Nuclear, Particle and Radiation Physics

The Impact of Re-homogenisation for Nodal Cross-section Corrections in OSCAR-4 as Applied to SAFARI-1 Research Reactor

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Abstract. Calculational support to the operation of the SAFARI-1 research reactor at Necsa is primarily performed with the in-house developed OSCAR-4 nodal diffusion code. Nodal diffusion methods implement a series of non-linear corrections to the nodal cross-sections. Such corrections are needed since nodal cross-sections are most often generated in a typical infinite assembly environment, as opposed to the actual core environment. In this work, the impact of one such correction method, termed nodal re-homogenisation, is evaluated for the case of the SAFARI-1 reactor. Furthermore, this is done with respect to a newly proposed OSCAR-4 SAFARI-1 core model. The new model is based in part on nodal cross-sections generated from the Monte Carlo based Serpent code, which supplies a consistent reference transport solution against which the capability of the non-linear model may be measured. The capability of the homogenisation model to correct for the environmental error is evaluated on an All-Rods-Out (ARO) SAFARI-1 fresh core. Such analysis is yet to be applied to research reactors. Traditionally, larger errors are tolerated in research reactors than in power reactors but due to increased commercial applications, it is of interest to get more accurate calculations. In this work, we show that the radial environmental error in k -eff for a SAFARI-1 core may be as large as 252 pcm with an average assembly power error of 2.30 %. When the re-homogenisation model is activated these errors are reduced to 88 pcm and 1.69 % respectively.

1. Introduction

In a nuclear system (e.g. in a nuclear reactor) the neutron distribution is governed by the Boltzmann transport equation [1]. Reactor design and analysis (in steady state) require an accurate determination of the neutron distribution, ideally obtained via the numerical solution of the steady state neutron transport equation. Various approximations are therefore applied in practical reactor analysis calculations using the typical deterministic calculation path which proceeds in two steps. The first step involves neutron transport calculations in fine energy groups in various material regions in the core, usually called nodes. This calculation produces average flux volume weighted cross-sections for each node. The second step is a global core nodal diffusion calculation using the average cross-sections obtained in the first step for each node in a reactor, producing core-wide flux and power distributions [2].

The errors are introduced through spectral energy condensation and spatial homogenisation. The errors introduced by using the diffusion approximation can largely be reduced by using the equivalence theory [3] in which the homogenisation process reproduces all node-averaged properties (reaction and leakage rates) of the heterogeneous reference solution [4].

However, even after the application of equivalence parameters, there still remain some errors due to the core environmental effects [1]. Spatial homogenisation and energy condensation (especially for fuel elements) are performed using approximate boundary conditions which do not correctly represent the core environment. For instance, the flux spectrum used for energy group collapsing and spatial homogenisation of the cross-section does not account for the effect of the adjacent assemblies, giving rise to environmental errors in the reactor calculation solutions. However, typical deterministic codes have in-built mechanisms designed to correct for these environmental errors.

While it is possible to get cross-sections for non-fuel elements in their correct environment, it is not practical to do so with fuel elements because fuel elements are moved around the core from cycle-to-cycle for the duration of their life in the core. Therefore fuel cross-sections are typically generated in an infinite fuel environment. In this work, we try to address the environmental errors associated with fuel cross-sections. In particular, we focus on the re-homogenisation correction mechanism in the OSCAR-4 code system used for the reactor analysis of the SAFARI-1 research reactor. This correction mechanism in OSCAR-4 was designed specifically for use in power reactors. Nevertheless, in this work we quantify the radial environmental error in the SAFARI-1 reactor and evaluate the efficiency and applicability of this mechanism in the Materials Testing Reactor (MTR) due to the approximate fuel environment.

2. The SAFARI-1 Research Reactor

The reactor consists of a 8 row x 9 column rectangular core lattice which contains 26 fuel assemblies and 6 fuel-follower type cadmium control assemblies and a number of reflector assemblies. The reactor uses plate type fuel assemblies using Low Enriched Fuel (LEU), 19.75 % enriched of the U_3Si_2Al type.

3. Theory

Deterministic calculational tools have emerged to be the standard for in-core neutronic analyses [4] e.g. core-reload and core-follow type calculations. Due to their efficiency, nodal diffusion based methods, whose formulation is based on nodal expansion methods [5] and the Analytic Nodal Methods are the main workhorse for such work. They are characterized by distinct features namely: node-averaged group fluxes and surface averaged partial (or net) currents, transverse integration (to get 1D diffusion equations) and the spatial dependence of the transverse leakage term. The 1D diffusion equations are used to relate surface currents and nodal fluxes [7].

The nodal diffusion equation can be written as

$$-\nabla D_g^n(r) \nabla \phi_g^n(r) + \Sigma_{t,g}^n(r) \phi_g^n(r) = Q_g^n(r) \quad (1)$$

where, $D_g^n(r)$ is the group diffusion constant in node n , $\phi_g^n(r)$ is the group average flux in the node, $\Sigma_{t,g}^n(r)$ is the average group total cross-section in the node, $Q_g^n(r)$ is the average in-group source in the node and g is the energy group. The homogenized nodal parameters are given by:

$$\Sigma_{x,g}^n = \frac{\int_{v_n} \Sigma_{x,g}(r) \phi_g(r) d^3r}{\int_{v_n} \phi_g(r) d^3r} \quad (2)$$

and

$$D_g^n = \frac{-\int_{s_n} \bar{n} \cdot \bar{J}(r) d^2r}{\int_{s_n} \bar{n} \cdot \phi_g(r) d^2r} \quad (3)$$

where $\Sigma_{x,g}^n$ is the macroscopic cross-section for general interaction, x , which represents either a scattering, absorption or fission reaction. Equation 2 and Equation 3 give the homogenized nodal cross-section and diffusion parameter respectively, where v_n and s_n are the node volume and node surfaces respectively. Equation 1 can be transversely integrated (over the directions perpendicular to the direction of interest) to get the 1D nodal diffusion equation which can be written as

$$-D_g^n \frac{d^2}{du^2} \Phi_{g,u}^n(u) + \Sigma_{t,g} \Phi_{g,u}^n(u) = Q_{g,u}^n(u) - L_{g,u}^n(u), \quad (4)$$

where $\Phi_{g,u}^n(u)$ is the average transverse-integrated flux in the direction u , $Q_{g,u}^n(u)$ is the average transverse-integrated group source in direction u and $L_{g,u}^n(u)$ is the transverse leakage term in direction u . Equation 4 is the nodal 1D equation, which can be solved analytically (i.e. the analytic nodal method).

As indicated above, nodal methods are mainly characterized by the relationships between the flux inside a node and the currents on the node surface, making them susceptible to the boundary conditions. We call this environmental impact. However, extensions to their formalism is an area of active research e.g. environmental correction mechanisms such as radial re-homogenisation.

3.1. Re-homogenisation

The nodal diffusion calculation is performed using assembly averaged cross-sections and discontinuity factors that enable equivalence between the heterogeneous and homogeneous geometries [8]. As discussed in section 1 these parameters are obtained from 2D single assembly transport calculation with reflective boundary conditions, hence they do not account for current assembly environment. As proposed by Smith [6] a re-homogenisation approach is suggested to determine the effect of this new environment on the approximate cross-sections generated from the infinite environment.

In the heterogeneous assembly calculation, the effects of flux shape changes on the homogenized cross-sections are determined and tabulated. The homogenized cross-sections are adjusted in the global diffusion calculation using the global flux shape and the tabulated correction factors from the transport calculation as shown as follows:

$$\bar{\Sigma} \approx \bar{\Sigma}_{x,g}^{n,0} + \Delta \Sigma^{rehom} \quad (5)$$

where $\bar{\Sigma}_{x,g}^{n,0}$ is the same as in equation 2, calculated in a infinite assembly and

$$\Delta \Sigma^{rehom} = \frac{1}{\bar{\phi}^{hom}} \sum_{r=x,y} \sum_{l=1}^L R_r^l a_r^l \quad (6)$$

is the cross-section correction factor, $\bar{\phi}^{hom}$ the average homogeneous flux, R_r^l are the Legendre coefficients representing the shape of cross-sections determined from the lattice calculation and a_r^l are the Legendre coefficients for inter nodal flux, determined in the nodal calculation. As described here, the re-homogenisation correction represents a relatively minor adaptation to any existing transversely integrated nodal code.

4. Methodology

4.1. Computational Tools

OSCAR-4 is a code system [9] developed and used at Necsa for the calculational support of the SAFARI-1 reactor, in terms of core-follow and reload calculations, as well as other safety analyses. OSCAR-4 employs the deterministic calculational path described above, utilizing transport solvers for cross-section generation with spatial homogenisation and spectral condensation and the full core nodal diffusion solver for the global solution. The OSCAR-4 code system consists of several independent codes, each with a specific function.

Multi-group homogenized nodal diffusion parameters are produced through the HEADE code. HEADE is a low order collision interface current transport solver, utilizing a response matrix formalism to solve a 2D fine-group transport problem for a given assembly type in an idealized (infinite) environment [10].

MGRAC performs global multi-group nodal diffusion and depletion calculations using the Multi-group Analytic Nodal Method (MANM) [11] as the primary solution method. MGRAC is the primary code used to simulate the operation of the reactor cycle. In addition to HEADE and MGRAC, there are several utility codes in OSCAR-4, used for various functions, including creating and updating of homogenized cross-section libraries.

Serpent [12], a 3D, continuous-energy Monte Carlo neutron transport code, was used to produce a reference solution and accurate homogeneous nodal cross-sections for non-fuel assemblies. Although a Serpent calculation is expensive, it was selected because Monte Carlo calculations are generally very accurate.

4.2. Model Construction

The construction of the Serpent-based OSCAR-4 SAFARI-1 model follows a particular philosophy associated with the OSCAR-Serpent link. This modelling approach entails, firstly, the development of a SAFARI-1 3D Serpent model, based on the engineering description of the reactor. Thereafter, a selection of relevant full-core 2D axial cuts of the SAFARI-1 core is taken from this 3D Serpent model, representing the various levels of axial heterogeneity present in the core. Cross-sections are generated on a spatial grid in accordance with the full-core nodal diffusion model. In this work, a 2D centre-line cut for an All-Rods-Out (ARO) model with fresh fuel assemblies was selected.

Full-core 2D Serpent calculations for this full-core 2D slice were performed, generating in the process the set of nodal equivalence parameters for each node (assembly) present in the 2D cut. It should be noted here that these parameters are generated from their correct environment in this present calculation and therefore no environmental error is present.

The nodal parameters were then taken into MGRAC. No environmental error is introduced at this stage and based on the equivalence theory mentioned in Section 1, MGRAC should reproduce the reference solution.

Fuel nodal parameters were then generated from HEADE in an approximate (infinite) environment using reflective boundary conditions. These nodal parameters were taken into MGRAC, replacing the exact nodal parameters for fuel only. The use of an infinite lattice environment introduces an environmental error associated with the fuel cross-sections. The HEADE based fuel models are generated with reflective boundary conditions around the fuel element. This is still a reasonable approximation for fuel elements because they are mostly surrounded by other fuel assemblies.

A full-core 2D calculation was repeated with and without cross-section re-homogenisation to quantify the environmental error thus introduced and to determine the efficiency of the correctional mechanism in the selected case.

5. Results and Discussions

The effects of the infinite fuel approximation and subsequent use of the re-homogenisation correction mechanism in OSCAR-4 for the full core ARO case were evaluated based on the k-eff values and relative power distribution as summarized in Table 1.

Table 1: k-eff and power errors for various 2D cases

Model	k-eff	Error (pcm)	Average Power Error (%)	Maximum Power Error (%)
Serpent	1.30402			
MGRAC (Equivalent)	1.30306	-74		
MGRAC (Infinite fuel)	1.30634	252	2.30	4.49
MGRAC (Infinite fuel + re-homogenisation)	1.30421	88	1.69	3.52

Serpent generated cross-sections achieved equivalence in MGRAC albeit with a small error in k-eff of 74 pcm. Since Serpent is a Monte Carlo code, some statistical variance will always be present. It should be noted here that there were no significant power errors between the Serpent reference case and the MGRAC equivalent solution because of equivalence. The rest of the cases are compared to MGRAC (Equivalent). In full core analysis, core follow calculations strive for a error of about 500 pcm. Therefore an error of 252 pcm is noticeable.

The table shows that the use of infinite fuel approximation introduces significant errors; 252 pcm error and maximum power error of 4.49 %. The re-homogenisation mechanism reduced both the error in k-eff and the maximum power error significantly.

Table 2 (a) and (b) shows the full-core relative power distribution from the reference solution (in bold). Table 2 (a) shows (in brackets) the relative power errors obtained from using the infinite fuel approximation while Table 2 (b) shows (in brackets) the relative power error obtained when using the infinite fuel approximation together with the re-homogenisation correction mechanism.

Table 2 (a) shows that significant power errors are found in positions C5, C7, E5, E7, G5 G7 including position C6 and D7. The first six are control rod positions where in this case we have fuel followers (since this is an ARO case). Fuel followers have different geometry from the normal fuel elements and as expected they show significant environmental effects. The big large errors in position C6 and D7 were possibility due to their unique surroundings i.e. close to a fuel follower and water again causing heightened environmental effects. The errors in the fuel followers were reduced quite significantly as indicated in Table 2 (b) by more 35 %. In position C6 (fuel) there was a 10.2 % reduction in error because fuel is more homogeneous.

It is notable however, that re-homogenisation did not reduce the errors in all the positions. In some positions i.e. B3, C4, D3, E4, G4 and G6, the errors actually increased. Re-homogenisation reduced the errors in some positions and increased the errors in some. However, the overall effect was a reduction in the full core environmental error.

6. Conclusion

We managed to quantify the environmental error associated with the SAFARI-1 full core ARO model. The infinite fuel approximation introduced 252 pcm difference in k-eff, and 2.30 % average power error. The re-homogenisation model reduced these errors to 88 pcm and 1.69 % respectively. The fuel followers show a greater sensitivity to environmental effects than the normal fuel elements. We conclude that the existing re-homogenisation model can potentially

Table 2: Assembly averaged relative power distribution for the reference ARO case with relative power errors for (a) the infinite fuel approximation and (b) the infinite fuel with re-homogenisation

(a) Infinite fuel approximation							(b) With re-homogenisation						
	3	4	5	6	7	8		3	4	5	6	7	8
B	2.57 (0.39)	2.71 (1.85)	3.20 (1.56)		2.68 (2.61)		B	2.57 (0.78)	2.71 (1.50)	3.20 (0.31)		2.68 (0.00)	
C		3.45 (1.74)	2.76 (3.99)	3.83 (3.92)	2.16 (3.24)	2.59 (2.70)	C		3.45 (2.65)	2.76 (2.26)	3.83 (3.52)	2.16 (1.91)	2.59 (1.50)
D	3.86 (0.78)	3.73 (2.41)	4.42 (1.81)		3.68 (3.53)		D	3.86 (1.04)	3.73 (1.92)	4.42 (1.11)		3.68 (1.57)	
E		4.16 (2.40)	3.34 (4.49)	4.65 (3.01)	2.60 (3.85)	2.82 (2.48)	E		4.16 (3.20)	3.34 (2.51)	4.65 (3.13)	2.60 (2.40)	2.82 (2.08)
F	3.84 (0.78)	3.67 (2.18)	4.38 (2.05)		3.66 (3.01)		F	3.84 (0.79)	3.67 (1.67)	4.38 (1.57)		3.66 (1.33)	
G		3.28 (1.22)	2.66 (3.76)	3.54 (2.54)	2.13 (3.76)	2.33 (2.15)	G		3.28 (1.85)	2.66 (1.56)	3.54 (2.75)	2.13 (1.95)	2.33 (1.68)
H	2.17 (0.92)	2.23 (1.35)	2.47 (1.21)	2.33 (0.43)	2.09 (1.44)		H	2.17 (0.91)	2.23 (0.91)	2.47 (2.00)	2.33 (0.43)	2.09 (1.42)	

be used in the research reactor environment. However this conclusion was arrived at based on the average core values. There is therefore need for a more detailed analysis of various mini-core cases e.g. a fuel assembly next to water, or a fuel assembly next to a control rod, to get a full understanding of the scenarios where the current re-homogenisation mechanism in OSCAR-4 works.

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Division F – Applied Physics

Experimental evaluation of emission models from a thermal evaporation source

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Abstract. Thermal evaporation is a well-known phenomenon used to produce metallic thin films for many industrial and research applications. Generally the focus is not on the evaporation rate, but the deposition rate which can be measured using a quartz crystal microbalance (QCM). In this study the interest is in the evaporation process, for which well-known models such as the Hertz-Knudsen equation exist but are not always accurate. A novel approach was developed to use the deposition rate on a QCM to study the evaporation flux from a surface. This required a model for the angular distribution of evaporating atoms in order to link the measured deposition rate to the evaporation rate. The literature generally assumes a point source with a $\cos^n \varphi$ angular dependence and $n = 0, 1, 2$ etc corresponding to isotropic emission, cosine emission associated with Knudsen effusion cells and more directed emissions, respectively. To measure low evaporation rates the model considers evaporation from a surface placed so close to the QCM that the assumption of a point source is questionable. Since a treatment of the evaporation rate from an extended source was not found in literature, a model was developed by treating the extended surface as many point sources and integrating numerically. The fraction of evaporated atoms incident on the QCM for point and extended circular sources for $n = 0, 1, 2$ and 3 are compared. The results also predict how the deposition rate should change with the distance between source and QCM. This is compared to data measured for the evaporation of antimony from a custom designed resistance heater in an ultrahigh vacuum environment to determine the most suitable emission model.

1. Introduction

The production of thin films is of great importance in research and industrial applications as diverse as the growth of conducting layers in microelectronics [1] to the coating of the mirrors of optical telescopes [2]. Various physical vapour deposition (PVD) techniques exist where the process of evaporation is the source of the deposited material [3]. Generally the focus is on the deposition rate, since these techniques are end-product driven. The fundamentals of evaporation can, however, be investigated using the equipment employed in these techniques. These fundamentals are of importance where the surface loss of samples due to evaporation takes place during sample surface characterization.

In this study the deposition rate of pure Sb, as measured by a quartz crystal microbalance (QCM) commonly employed in PVD techniques was used to relate the amount of deposited material measured to the actual amount of material that evaporated from the evaporation source. This required a model for the angular distribution of evaporating atoms in order to link the measured deposition rate to the evaporation rate.

2. Theory

2.1. Point source

Deposition of thin films involves consideration of both the characteristics of the evaporation source and the orientation and placement of the substrate upon which the evaporated atoms or molecules impinge. In addition, only a fraction of the evaporant leaving the sample surface impedes on the quartz crystal. Evaporation from a point source is the simplest of situations to model and the details are well-known [4]. Consider a point on a surface from which particles are evaporating. The particles may leave with equal probability at any angle (isotropic), or they may follow the so-called cosine law often used for Knudsen cells. The particles may even be directed more strongly upwards from a deep narrow crucible. In general one may assume that the particles leave a point on the surface with an angular dependence $\cos^n \varphi$ where φ is the angle relative to the surface normal. Figure 1 illustrates this.

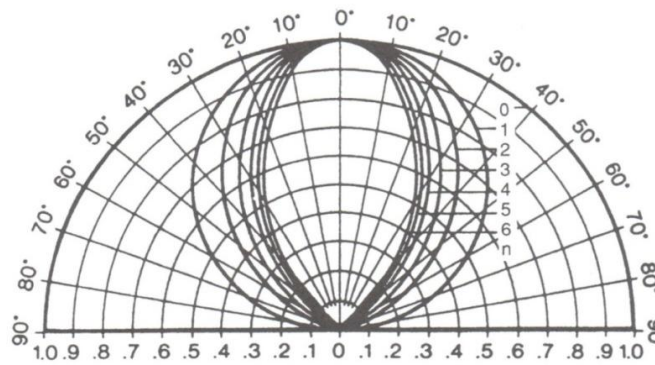


Figure 1. Calculated lobe-shaped vapour clouds using the cosine law $\cos^n \varphi$ where φ is the angle relative to the surface normal at that point: $n = 0$ corresponds to the isotropic case, while $n = 1$ is a simple model for a surface or Knudsen cell, and $n = 2$ or higher correspond to more directed anisotropic sources applicable for a narrow deep evaporation crucibles [4].

In a case where n is large, the vapour flux is highly directed. Physically n is related to the evaporation crucible geometry and scales directly with the ratio of the melt depth below the top of the crucible to the melt surface area [4]. More specifically in the case of this study n is related to the sample holder geometry.

If the particle path makes an incidence angle θ relative to the normal of the collecting surface a distance r away, then the mass per unit area deposited on the substrate is $\frac{M_e(n+1)\cos^n \varphi \cos \theta}{2\pi r^2}$ where M_e is the total evaporated mass [4] and hence the fraction of particles collected on an area A_s is given by

$$\int_{A_s} \frac{(n+1)\cos^n \varphi}{2\pi} \frac{1}{r^2} \cos \theta dA_s. \quad (1)$$

Equation 1 can be applied to a flat collecting surface (see figure 2a) lying a distance h directly above and parallel to the emission point. Then the angles φ and θ are equal, with $\cos \varphi = \cos \theta = h/r$. If the collecting area is a disk of radius r_s directly above the emission point then the expression becomes

$$\int_{l=0}^{r_s} \frac{(n+1)\cos^{n+1} \varphi}{2\pi} \frac{1}{r^2} (2\pi l dl) \quad (2)$$

and noting that $r = \sqrt{h^2 + l^2}$, integration gives the fraction of collected particles as

$$1 - [1/(1 + (r_s/h)^2)]^{\frac{(n+1)}{2}}. \quad (3)$$

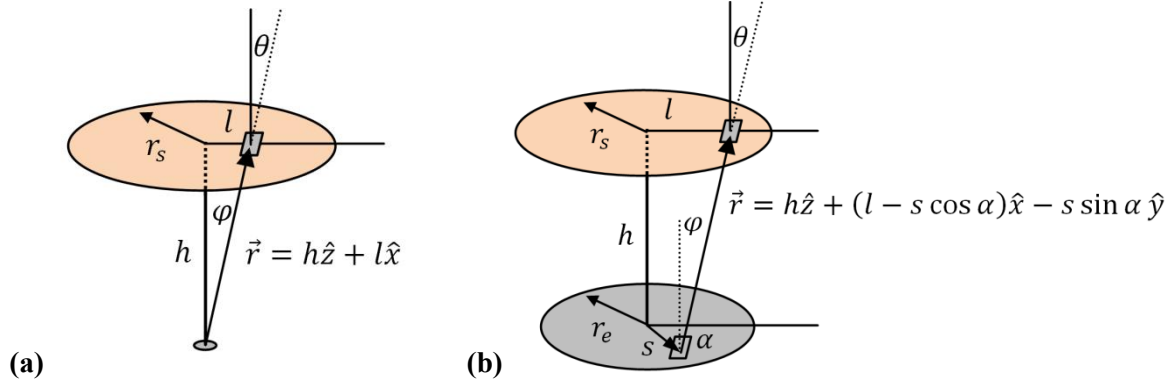


Figure 2. (a) Particles evaporating from a point on a surface and being collected on a disk of radius r_s that is a distance h directly above the point source. (b) Particles evaporating from an extended disk surface of radius r_e and being collected on a disk of radius r_s that is a distance h directly above the extended source.

2.2. Extended source

Consider now evaporation not from a point source, but rather from a distributed region or surface area. This leads to a situation as shown in figure 2b. Taking the total evaporating region as a disk of radius r_e directly below and parallel to the collecting disk, equation 2 needs to be modified by considering how the value of $(\cos^{n+1} \varphi)/r^2$ varies as the emission point $(x, y) = (s \cos \alpha, s \sin \alpha)$ moves over the surface of the emitting disk. This results in a new model for evaporation from an extended surface given by

$$\int_{l=0}^{r_s} \frac{(n+1)}{2\pi} \left[\frac{1}{\pi r_e^2} \iint_{A_e} \frac{\cos^{n+1} \varphi}{r^2} dA_e \right] (2\pi l dl). \quad (4)$$

In this case $r = \sqrt{h^2 + (l - s \cos \alpha)^2 + (s \sin \alpha)^2}$, so equation 4 can be rewritten as

$$\frac{(n+1)h^{n+1}}{\pi r_e^2} \int_{l=0}^{r_s} \int_{\alpha=0}^{2\pi} \int_{s=0}^{r_e} \frac{sl}{[h^2 + (l - s \cos \alpha)^2 + (s \sin \alpha)^2]^{\frac{(n+3)}{2}}} ds d\alpha dl \quad (5)$$

which may be evaluated numerically.

3. Experimental setup and procedure

A sample stage manipulator and an Inficon XTC/3s QCM were fitted to an Auger Electron Spectroscopy (AES) system. This allowed the user to reposition a sample mounted on a resistance heater from a position in front of the electron gun/analyser to a position underneath the QCM, as illustrated in figure 3. Not only can the sample surface thus be analysed before an evaporation experiment is performed, but also the surface can also be sputter cleaned from any contaminants that might influence the evaporation rate.

A 99.999% pure Sb disk was used as an evaporation sample. The AES system was evacuated to a base pressure of 3×10^{-8} torr, and after heating the sample to 673 K the average evaporation rate as measured by the QCM over a time interval of 1 min was recorded for various separation distances between the samples surface and the QCM, which was set accurately using a micrometer and varied between 0.5 cm and 3.0 cm for the measurements.

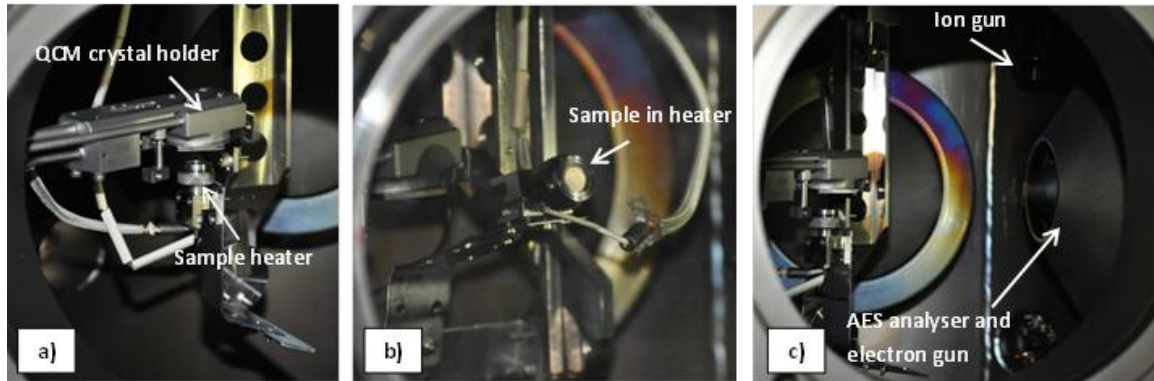


Figure 3. The different parts of the modifications made and how they relate in terms of position to each other: **(a)** The QCM crystal holder with the sample heater positioned under it for an evaporation run. **(b)** The sample being moved by means of a manipulator and rotated towards the AES analyzer shown in **(c)**.

4. Results and discussion

The fractions of collected particles were theoretically calculated for the experimental conditions ($r_e = 0.395$ cm and $r_s = 0.4125$ cm) using equation 3 for a point source and equation 5 for an extended source for various angular distributions (n) and separation distances (h). For the numerical evaluation of equation 5, the Matlab function ‘triplequad’ was used. This data is given in table 1.

Table 1. Percentage of emitted particles from an evaporation source with $\cos^n \varphi$ point angular distribution that is incident on a circular capturing surface of radius $r_s = 0.4125$ cm at a distance h directly above it.

h (cm)	Point source				Extended source ($r_e = 0.395$ cm)			
	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 0$	$n = 1$	$n = 2$	$n = 3$
0.5	22.86%	40.50%	54.10%	64.60%	18.95%	32.37%	42.12%	49.40%
1	7.56%	14.54%	21.00%	26.97%	6.94%	13.03%	18.41%	23.17%
1.5	3.58%	7.03%	10.36%	13.57%	3.42%	6.63%	9.64%	12.47%
2	2.06%	4.08%	6.06%	7.99%	2.01%	3.94%	5.80%	7.59%
2.5	1.33%	2.65%	3.95%	5.23%	1.31%	2.59%	3.84%	5.05%
3	0.93%	1.86%	2.77%	3.68%	0.92%	1.83%	2.71%	3.59%
3.5	0.69%	1.37%	2.05%	2.72%	0.68%	1.35%	2.02%	2.67%
4	0.53%	1.05%	1.57%	2.09%	0.52%	1.04%	1.56%	2.06%
4.5	0.42%	0.83%	1.25%	1.66%	0.42%	0.83%	1.24%	1.64%
5	0.34%	0.68%	1.01%	1.35%	0.34%	0.67%	1.00%	1.34%

As expected, the collected fractions for an extended source are always smaller than the corresponding value for a point source, although the differences become negligible for larger separations. For both the point source and extended source models, the collected fraction increases with increasing n which corresponds to more directed evaporation.

The experimentally measured deposition rates and the theoretically calculated fractions of collected particles cannot be compared directly. To test which theoretical model best corresponded to the experimental results, all sets of data were normalized relative to a fixed separation distance, namely $h = 3$ cm which was the maximum experimental value used. The relative change in the experimental deposition rate should then be directly comparable to the relative change in the collected fraction of the theoretical models as the separation distance is varied. The comparison is shown in figure 4, where the horizontal axis giving the separation distance is given on a log scale.

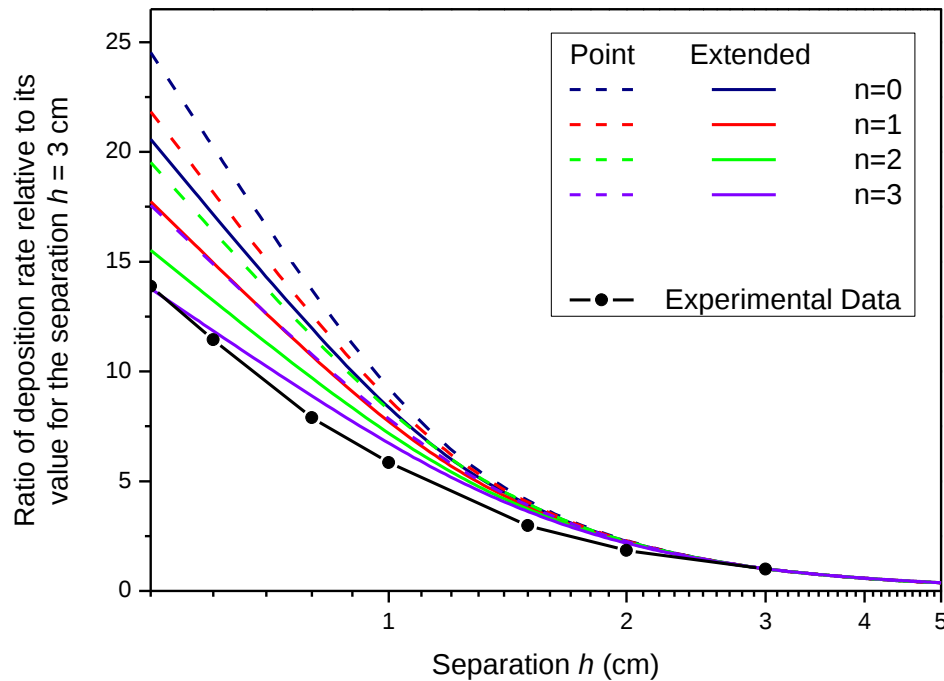


Figure 4. Comparison of the relative experimental deposition rate as a function of separation distance compared to the relative collected fraction using various models.

As the separation decreases, the relative collected fraction based on the theoretical calculations increases faster for the point sources compared to the extended sources for the same n value, because for the extended sources it is more likely for some particles to pass outside the collecting surface. Also, for both the point and extended sources, the relative collected fraction increases faster with decreasing separation distance for the less directed emission distributions (smaller n values). The least increase in relative collection fraction with decreasing separation distance occurs for an extended source of high directionality (large n), and this corresponds best to the experimental observations made for the evaporation of Sb. Although the form of the experimental curve and the theoretical curves do not match very well, it is clear that the experimental data coincides better for the evaporation model from an extended source and for high directionality (n).

5. Conclusion

The results show that assuming the Knudsen model ($n = 1$) for point sources can lead to serious errors when considering evaporation and that the new evaporation model for an extended source and for high directionality (n) provides a better fit to the experimental data in the case of evaporation of antimony from a custom designed resistance heater in an ultrahigh vacuum environment. This evaporation model best fitting the experimental data predicts how the deposition rate should change with the distance between the source and QCM and provides the necessary link of the most suitable emission model which is necessary to study evaporation rates by using measurements of deposition rates.

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Handheld QKD Device using the COW Protocol

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Abstract. Quantum Key Distribution (QKD) is an emerging field of information security. To date, this technology has been implemented for large scale financial and voting purposes, but QKD is a versatile solution which can also be utilised to secure personal transactions. The development of low cost, portable QKD devices can further promote the use of quantum encryption in commercial security systems. The proposed device uses the Coherent One Way (COW) protocol to exchange a secret key between two authenticated parties. An advantage of using the COW protocol is the small size and low cost of the setup. This is ideal for a hand-held device used for short-range QKD. The design of the system, in particular, the conversion from a fibre channel to a free space channel, and the synchronisation of the system will be discussed.

1. Introduction

The security of data transmissions is an evolving technology. Standard security protocols rely on a pseudo-random number generator or the complexity of a mathematical algorithm, but with increasing computing power, these protocols become obsolete [1]. Sensitive data that requires long-term security can also be intercepted during transmission and stored until the necessary technology to decrypt it is developed [2]. Long-term data security is, therefore, necessary in order to preserve sensitive data against increasing decryption power. Quantum Key Distribution (QKD) is a symmetric key sharing technology which exploits the principles of quantum physics to ensure a theoretically secure communication between two authenticated parties. The Uncertainty Principle [3] and ‘No Cloning’ theorem [4] of quantum physics facilitate the use of quantum particles as bits which can neither be prematurely measured nor copied without introducing an observable error in the transmission. QKD, therefore, provides an effective means of sharing a secret key without the risk of an adversary copying and storing this key.

The most commonly used QKD protocols e.g. BB84 [5] and SARG04 [6], encode each single photon with a qubit using polarisation or phase differences. These discrete variable protocols employ the use of two orthogonal bases, each providing two states to be used as a bit. As part of the protocol, the receiver is required to randomly choose the basis of measurement for each single photon. For

instances in which the wrong basis was chosen, the bit must be discarded. Distributed phase-reference protocols can improve on the efficiency of the key sifting process [7]. These protocols are also simpler to implement and require fewer components, hence decreasing the risk of Trojan horse attacks [8]. Section 2 describes distributed phase reference protocols, focusing on the coherent one-way protocol. Section 3 discusses the use of portable, personal QKD devices and the current literature. Section 4 presents the experimental setup and Section 5 discusses the synchronization of the system in detail.

2. The Coherent One-Way Protocol

Distributed phase reference protocols provide a simpler and more practical key distribution [9]. This class of protocols uses a faint, coherent light source and does not require a perfect single photon source. Confirming the coherence of the beam after transmission serves as a method to ensure the security of the transmission. The Differential Phase Shift (DPS) [10] and Coherent One-Way (COW) [11,12] protocols are the most common distributed phase reference protocols. The system described in this paper utilises the COW protocol.

The Coherent One-Way (COW) protocol does not encode bits using non-orthogonal bases in the form of polarisation or phase differences. The bit encoding, chosen by Alice, the transmitter, is distributed over two consecutive pulses [9]. One pulse contains a single photon and the other must be empty. The order of the empty and non-empty pulses determines the quantum bit (qubit) value, such that

$$|0_k\rangle = |\sqrt{\mu}\rangle_{2k-1} |0\rangle_{2k} \quad (1)$$

and

$$|1_k\rangle = |0\rangle_{2k-1} |\sqrt{\mu}\rangle_{2k} \quad (2)$$

where μ is the mean photon number and k is the time bin index. The receiver, Bob, measures each pulse to determine the presence of a photon and he keeps a record of the time of arrival of each pulse so as to resolve the pulses into their respective bits. Therefore, the security of this protocol does not depend on the random choice of a measurement basis, as in most protocols. Instead, the coherence of the laser pulses is used as a means to ensure the security. A portion of the pulses are diverted into an unbalanced interferometer and measured on a separate monitoring detector. The monitoring line is used to detect two consecutive non-empty pulses, utilised as decoy states. When these pulses enter the unbalanced interferometer in Bob's apparatus, they should interfere constructively at one output and destructively at the other. If this is compromised, it indicates the presence of an eavesdropper. The coherence of the pulses can be monitored in real time or as part of the post-processing and it does not affect the key generation. Monitoring the coherence between the decoy pulses means that an eavesdropper cannot perform a photon number-splitting (PNS) attack without disturbing the monitoring line and being detected by Bob [9]. A PNS attack performed coherently over the bit separation will still produce observable errors in the coherence within a decoy state [9]. The COW protocol was experimentally realized over a 150 km optical fibre by Stucki et al [13].

3. Personal QKD Devices

QKD technologies have been commercially developed for metropolitan fibre optic networks [14,15] and research and development of free space quantum networks is still ongoing [16]. Both these commercial applications focus on extending the channel length of a QKD network by exploiting node-hopping techniques or by optimising the visibility of the channel. Short-range commercial devices have recently been developed for use with ATMs [17]. This extends the commercial use of QKD to portable personal devices. Such devices can be used to exchange a secret top-up key between a user (Alice) and their bank at a central node, such as an ATM (Bob). The ATM would, in turn, exchange a

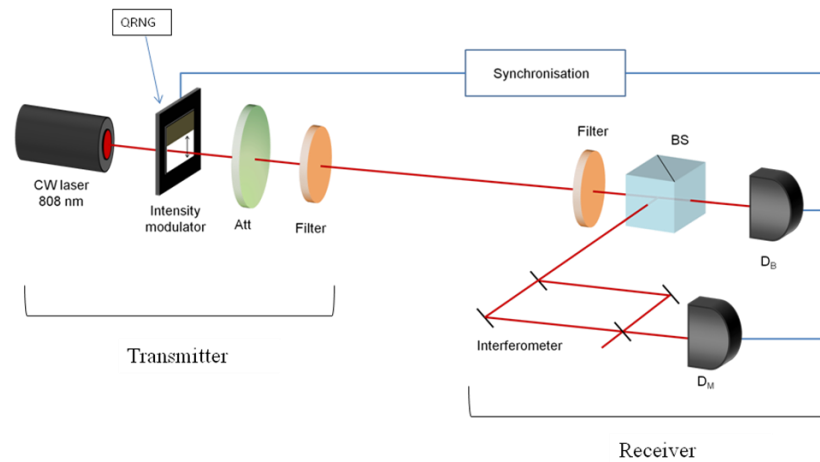


Figure 1: The free-space adaption of the COW protocol includes an 808 nm continuous wave laser which is modulated and attenuated to form a train of pulses. The pulses are filtered and transmitted to the receiver and measured by the primary detector, D_B . A beamsplitter extracts a portion of the pulses and diverts them into the monitoring line. The pulses are passed through an unbalanced interferometer and a detector D_M is positioned at the deconstructive interference output. Should D_M fire, the presence of an eavesdropper is inferred.

key with the bank, allowing the user to then use the key for personal transactions with the bank requiring a One-Time Pad (OTP), e.g. for internet banking. A device developed by Duligall et al

realises this short-range application [17]. This device uses the BB84 protocol with polarization encoding to exchange a key between portable Alice and Bob modules. In the Bob module, a holographic diffraction grating was used to transmit any incoming photon directly into one of four detectors, each measuring one of the four polarization states. This replaces the 50/50 beamsplitter and polarization beamsplitters which usually direct a photon to the detectors in the setup of the BB84 protocol. The modification reduces the efficiency of the protocol from 50% to 25% in exchange for a smaller device and lower cost. A micro-optic Alice module was developed by Vest et al to be fitted into handheld devices [18]. The module included four vertical cavity surface emitting lasers each coupled to a polariser and combined into one output via a waveguide chip. The device was able to produce pulses at 100 MHz and is being further optimized to reduce birefringence effect in the waveguide. The end product will be 25 x 2 x 1 mm, making it ideal for integration into devices such as cellphones. Both the above mentioned devices use polarization encoding and a randomly chosen measurement basis to produce a cryptographic key. This process can be simplified using the COW protocol, as discussed below.

4. Adapting the COW Protocol for a Free Space Device

The device proposed in this paper uses the COW protocol for a short-range, free space quantum key exchange, shown in Figure 1. The apparatus required by the user, Alice, is compact and easily portable. The device consists of a coherent, faint laser source, a beam modulator and an attenuator. The laser is passed through a mechanical modulator which assigns the bit allocation to each pulse. The beam is then attenuated to statistically contain no more than one photon per pulse. Additional apparatus for the Alice setup could include mirrors for alignment and wavelength filters to prevent stray light from entering the channel.

Bob's apparatus will be housed in a fixed location, serving as an intermediate node between the user and the service provider, e.g. the bank. This apparatus can, therefore, be larger than Alice's

apparatus. Bob's required components include a beam splitter, an unbalanced Mach-Zehnder interferometer and two single photon detectors. The train of pulses received by Bob is first passed

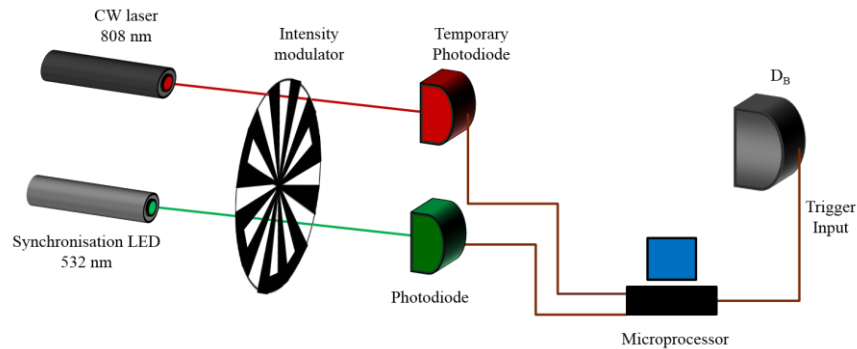


Figure 2: The 808 nm laser and green LED are both modulated by an optical chopper wheel. The laser is positioned at the outer edge of the wheel and is modulated by beam blockers on the wheel to form a fixed encoded sequence. The green LED is positioned near the center of the wheel and is not affected by the encoding. Both beams are measured by photodiodes and processed by an Arduino microcontroller which transmits the resulting trigger signal to Bob's detectors.

through a beam splitter which transmits most of the pulses to the primary detector. This measures the bits intended for the key generation. A portion of the beam is diverted into the monitoring line so that Bob can check the coherence of the beam. The diverted pulses pass through the unbalanced Mach-Zehnder interferometer so that two consecutive pulses interact at the output. Similar to Alice's setup, Bob will also need additional filtering to remove stray light, which can increase the dark counts measured by the detectors. The electronics required to synchronise the detectors to the incoming pulses is housed with Bob's apparatus.

5. Synchronisation of the System

For the proposed QKD system, Alice and Bob's clocks must undergo an initial synchronization. A green LED was included with Alice's apparatus to serve as the synchronization light source. The synchronization could have also been done with an electrical connection but this would require a plug-in connection between Alice and Bob and the components could deteriorate due to oxidation. An alternative synchronization could be done with a radio transmitter but an optical signal is lower on power consumption. The green LED was spatially filtered through an aperture so that the beam size is of the same dimension as that of the primary laser and was passed through the same pulse modulation. The pulses from the green LED were measured by a photodiode in Bob's apparatus. The resulting signal from the photodiode was transmitted to an Arduino microcontroller. The microcontroller measured and processed the signal before using it to trigger the detectors in real time. This method allowed for a simple synchronization system which was passive in Alice's apparatus.

For a proof of principle lab setup, an optical chopper wheel was used to mechanically modulate the beam. While using the wheel as a chopper is a cheaper solution, it is only appropriate for lab conditions since the bit allocation is fixed instead of randomly chosen. For the purpose of a proof of principle setup, the wheel still allows a complete evaluation of the quantum bit error rate, which is the key criteria of a QKD system. The green LED was positioned closer to the middle of the wheel, while the 808 nm laser beam is positioned at the outer edge of the wheel, as shown in Figure 2. This positioning creates similar pulse modulation in both beams while allowing the primary laser to undergo bit encoding independent of the green LED. Practically, some of the wheel apertures were strategically blocked at the edges so as to create a periodic bit sequence for the 808 nm laser but the

green synchronization signal was unaffected and continued to produce a steady pulse frequency. The positions of the primary laser and synchronization LED were finely adjusted so that the LED was blocked as the 808 nm laser was transmitted through Bob's apparatus, reducing any stray light in the detectors. The synchronization signal must, therefore, be inverted in order to trigger the detectors' gates to receive the laser pulses.

In order to precisely set the relative positions of the laser and the green LED, a temporary photodiode was installed to measure the primary laser. This signal from this photodiode was also transmitted to the Arduino microprocessor so that both the laser and synchronisation LED could be simultaneously monitored. Since the 808 nm laser was in a fixed position, aligned with the other components, the position of the green LED was adjusted until the voltage measurements from each photodiode were inversions of each other. The position of the green LED was also finely adjusted so that the beam is measured by the microprocessor before the arrival of the 808 nm laser. This time delay allows for the microprocessor to measure and invert the signal from the green LED and transmit the trigger signal to gate the single photon detectors. This is shown in Figure 3. The fixed, ten bit encoding for the 808 nm laser was added to the wheel with a repetitive sequence of 0110111001 and a correlation measurement was done. The results in Table 1 show that the green LED provided a stable trigger signal of 1010101010. The bit encoding can be measured whenever the trigger has a value of 1. The measured bits therefore show that the bit encoding was preserved while remaining synchronised with the trigger. For the COW protocol, two measured bits form one bit in the cryptographic key. Using equations 1 and 2, the resulting key is 1001. A decoy signal was also included to be measured by Bob in the monitoring line.

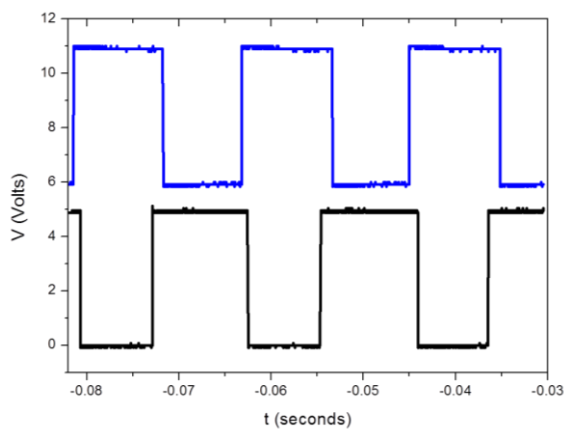


Figure 3: The blue and black lines represents the voltage output from the measurement of the 808 nm laser and the green LED respectively. The voltage signals were processed through an inverting comparator, hence, both are inverted in this figure. The LED is positioned so that it is measured before the 808 nm laser. This compensates for the time delay between the measurement of the LED and the trigger pulse being received at the detector gate. Both sets of data had voltage measurements between 0 V and 5 V. For illustrative purposes, the 808 nm pulses are displayed above the LED pulses.

Table 1: Time correlated measurements by the respective photodiodes of the 808 nm laser and the green trigger LED and the resulting bit sequence.

Trigger	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0
808nm	0	0	1	0	1	0	0	0	1	0	1	0	1	0	0	0	0	0
laser																		
Bits	0		1		1		0		1		1		1		0		0	
Key	1				0				decoy				0				1	

Conclusion

A handheld, free space QKD device has been designed using the COW protocol. The protocol provides a simple and practical method of generating a cryptographic key while maintaining security against photon number-splitting attacks by an eavesdropper. While the COW protocol was developed for fibre optic networks, it has been adapted for use in a short range free space device which will not

experience turbulence effects. A low-cost synchronisation system has been designed for the device. The simplistic design is passive in Alice's apparatus, requiring only a green LED as the trigger source. The LED was positioned to reduce stray light in the quantum channel. The synchronization system proved effective in providing a stable trigger for Bob's detectors while keeping the primary laser and the trigger source synchronized.

Acknowledgements

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Determining the effect of the solar cell band gap on power yield in southern African irradiance conditions

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Abstract. Solar panel yield is determined both by the local available solar irradiance and the detector characteristics. The Shockley-Queisser limit is the theoretical limit of maximum efficiency of any single junction solar cell. It is based on the maximum possible yield for the band gap of the junction in question and not on any practical or manufacturing limits. To a first approximation this limit is calculated for the irradiance at the top of the atmosphere. A more accurate calculation requires considerations of the solar ray attenuation at the specific site of measurement. The contributions to the irradiance are not proportionally the same on the surface of the earth as at the top of the atmosphere, as different wavelengths of incident light are scattered and absorbed differently. As such the optimal band gap on the surface of the Earth will slightly differ from that obtained from the first order approximation. Due to the variability of atmospheric conditions with time and geographical position, this optimal band gap will also vary with time, location and orientation. This paper calculates the optimum band gap for site specific parameters, such as latitude, altitude and aerosol types, descriptive of southern African sites identified for solar power generation. The paper highlights the key factors that influence the band gap optimisation, which would assist in the research and development of more efficient solar cells, under southern African atmospheric conditions and allow for more accurate predictions to be made for local solar power yield.

1. Introduction

The most widely used material for photovoltaic energy harvesting is doped silicon with n-type or p-type impurities [1]. There are many factors contributing to the efficiency of a photovoltaic solar cell. These factors can be intrinsic or non-intrinsic. Non-intrinsic factors such as reflection losses and electrical resistance could thus theoretically be eliminated through improved device design and manufacturing technology. Intrinsic factors are determined by fundamental physical laws, which cannot be avoided by advanced manufacturing techniques or other methods. This paper considers an ideal solar cell which accounts only for the intrinsic factors and assumes the non-intrinsic factors are negligible.

Efficiency in this paper is the percent of solar energy on the panel which is converted to electrical energy. William Shockley and Hans J. Queisser calculated the limit of the efficiency of a single p-n junction solar cell, known as the Shockley-Queisser limit or the detailed balance limit [2]. Theoretically this limit ranges from 30-33.5 % [2, 3, 4].

The Shockley-Queisser limit may vary with the types of losses in the atmosphere, which are largely dependent on the solar zenith angle, which in turn varies with time of day, time of year, geographical location and atmospheric composition. Most calculations use a single spectrum of solar irradiance at ground level, such as the NREL AM1.5 data [5-8] data which assumes a constant air mass of 1.5 and

does not account for any of these variations. In this paper the effect of these variations are calculated and analysed using a wavelength dependent solar irradiance model for conditions specific to the South African highveld, which has been tested against wavelength sensitive data for De Aar, Northern Cape.

2. Theory

The solar irradiation which reaches the surface of the earth is calculated from the extra-terrestrial solar irradiation by subjecting it to the extinction processes occurring due to the atmosphere [9]. The degree of extinction is a function of the beam's atmospheric path length, determined by the solar position. For this paper the solar position was calculated with the *Plataforma Solar de Almería* (PSA) algorithm [10]. The extra-terrestrial solar spectrum used was the synthetic/composite extra-terrestrial spectrum [11] and the extinction processes calculated according to the method laid out by Gueymard [9].

Photovoltaic cells function on the principle that electrons absorb incoming photons' energy, which raises their energy sufficiently to overcome the band gap to reach the conduction band. Photons having wavelengths that are larger than the band gap of the solar cell are not absorbed at all, whereas those having wavelengths much shorter than the band gap rapidly release heat to the lattice of the solid and therefore only the fraction of the photon's energy equal to the band gap is converted to electrical energy. The cut off energy for a solar cell is:

$$E_g = q V_g \quad (1)$$

where q is the electronic charge and V_g is the potential difference of the band gap.

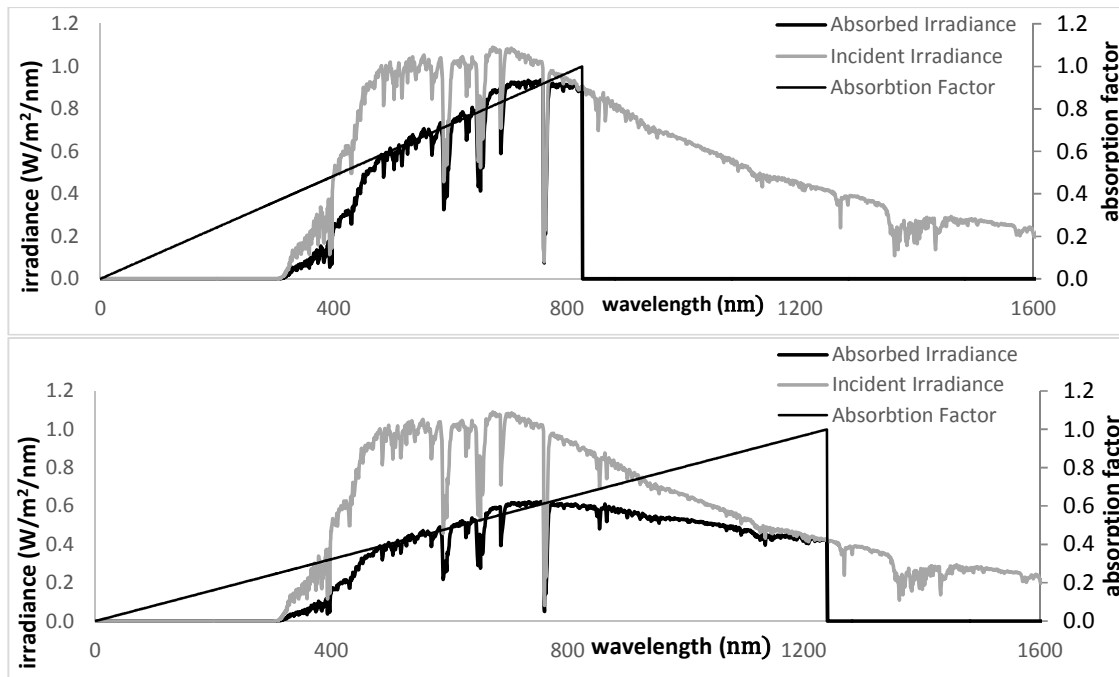


Figure 1: Comparison of the spectra of the radiation absorbed by ideal solar cells with 825 nm band gap (top) and 1250 nm band gap (bottom). The incident irradiance is that calculated for 10h30 21 June.

The irradiance absorbed by an ideal solar cell is simply the product of the incident irradiance and the absorption factor as in Figure 1. The absorption factor has the range 0 to 1 where 0 is no absorption and 1 is complete absorption (absorption factor = efficiency/100). In Figure 1 the absorption factor does not take into account any electron-hole recombination in the cell itself, thus it is sometimes referred to as the ultimate efficiency [2].

The ideal solar cell absorbs E_g for each photon with energy E_g or higher, while photons of lower energy will produce only heat but no electrical current. For an ideal single junction solar cell radiative recombination is the only cause of electron-hole-pair recombination. The loss due to radiative recombination is therefore proportional to the number of electrons and holes. The Fermi level describes the concentration of electrons and holes in a p-n junction at equilibrium. When a p-n junction is not in equilibrium, as is the case under solar irradiation, the work required to add an electron to each of the doped regions differs. These energy levels are distinguished from those at equilibrium and are referred to as quasi-Fermi levels [12].

In order to determine the radiative recombination rate, we take a solar cell in equilibrium with a surrounding blackbody radiation field at T_c (the temperature of the cell). In this system the electron quasi-Fermi level is equal to the hole quasi-Fermi level throughout the semiconductor from the detailed balance principle [2]. The solar cell is thus in thermal equilibrium and its radiation is calculated by the blackbody formula [2]. The rate of radiative recombination for zero difference between the quasi-Fermi level for the holes and that of the electrons is:

$$R_0 = \frac{2 \pi}{c^2 h^3} \int_{E_g}^{\infty} \frac{E^2 dE}{e^{E/kT} - 1} \quad (2)$$

where c is the speed of light, h is Planck's constant, k is Boltzmann's constant and T is the temperature of the cell.

For an ideal solar cell there is negligible recombination in the depletion zone of the p-n junction and so the difference between the quasi-Fermi levels for the holes and electrons is equal to the external voltage [12]. The lowest possible radiative recombination rate is:

$$R = R_0 q e^{(qV/kT)} \quad (3)$$

where V is the potential difference between the two electrodes.

The electron-hole pairs that are created and do not recombine generate electrical current across the junction. For an ideal solar cell in which all the solar photons possible are absorbed, and the only recombination is radiative recombination, the current density is given as:

$$J = q \left(N - R_0 e^{(qV/kT)} \right) \quad (4)$$

where N is the number of solar photons per second with energy above the solar cells band gap.

The power yield is the product of the potential difference between the two electrodes and the current. The optimum voltage to yield the maximum power is found using the generalized reduced gradient (GRG) method of iteration. This power integrated over that time interval gives the energy yield which is then divided by the solar energy incident on the panel over that interval; this gives efficiency. Figure 2 shows the absorption function for an ideal solar cell band gap of 1081 nm for a specific time as well as the ultimate efficiency for that band gap.

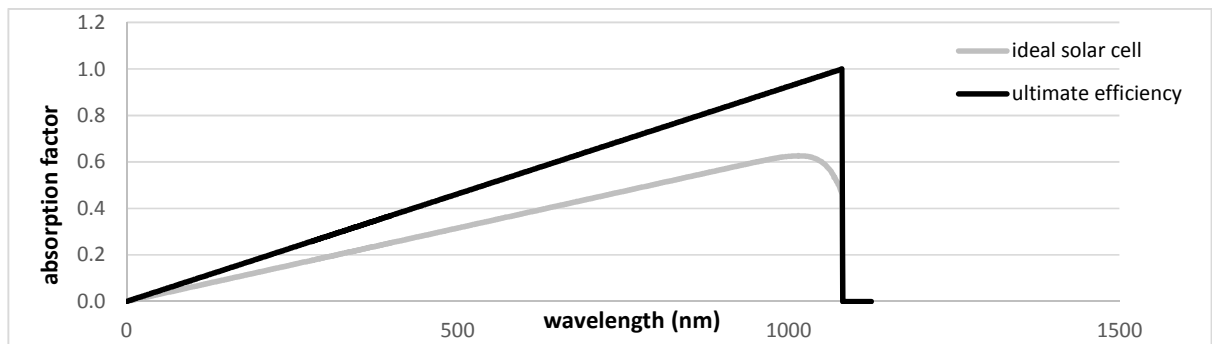


Figure 2: The absorption function for a solar cell that has the radiative recombination taken into effect calculated for De Aar at 10h00 21 June, with the ambient temperature of 10°C.

3. Procedure

A model for Southern African solar conditions was previously created and tested against available wavelength dependent data [13]. This model was used to calculate a solar spectrum with resolution of 1 nm at 10 minute intervals. In the current paper we consider the computationally simplest scenario of solar tracking panels, meaning that the panels always face the Sun. Furthermore, shading losses were neglected. The Shockley-Queisser limit for each of these spectra was calculated. Figure 3 displays these limits as the absorption factor (i.e. the fraction of the available energy) vs the band gap characteristic wavelength on the same set of axes for comparison.

In order to compare with the approach of [2, 3, 4], where a single reference spectrum is used to represent the whole day, an approximation of the yield was calculated at 10 minute intervals and added together. It was then recalculated using a single average spectrum for that day and the results compared.

The yield was calculated at 10 minutes intervals for the 21st day of each month from June to December. For each day the optimal band gap, the efficiency at that band gap, the efficiency for a 925 nm band gap and the percentage difference in energy yield was calculated for each month. These are shown in table 1.

4. Results

The Shockley-Queisser limit for different times of the day are plotted below for band gap equivalent wavelengths of 500 nm to 2500 nm with 0.04 eV step size and for 750 nm to 1750 nm with 0.0082 eV step size.

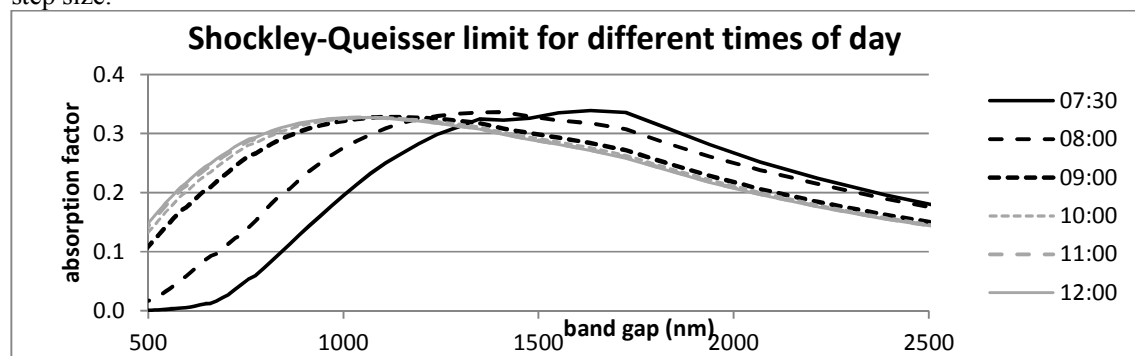


Figure 3: The Shockley-Queisser limit for different times of the day on 21 June at De Aar under clear sky conditions.

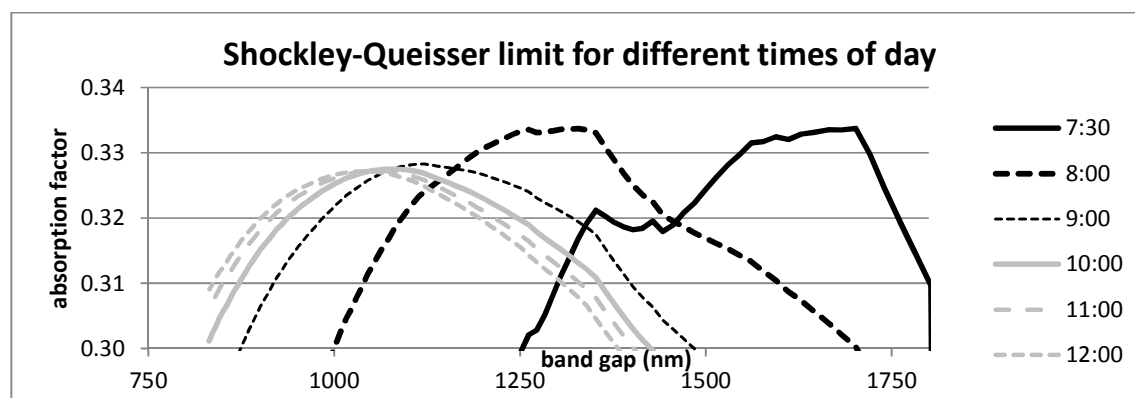


Figure 4: The Shockley-Queisser limit for different times of the day on 21 June at De Aar, under clear sky conditions, showing just the peaks and calculated at smaller intervals.

Table 1. Comparison of efficiency at the optimal band gap and at the 925 nm band gap.

Date	Efficiency for 925nm [%]	Optimal efficiency [%]	Optimal band gap [nm]	Increase in power [%]
2000/06/21	31.67	33.34	1089	5.3
2000/07/21	31.34	32.57	1089	3.9
2000/08/21	31.76	32.84	1089	3.4
2000/09/21	31.70	32.56	1073	2.7
2000/10/21	31.52	32.56	1105	3.3
2000/11/21	31.21	32.25	1105	3.4
2000/12/21	31.80	32.51	1066	2.2

When the yield was calculated at 10 minute intervals and added together the optimal efficiency was 33.34 % at 1089 nm band gap as in the table 1. The calculated solar irradiance was then first integrated and then the Shockley-Queisser limit calculated (the approach commonly used [2, 3, 4]) for the full day's spectrum, the peak efficiency calculated was 34.99 % at 1121 nm. There is a small difference in the position of the peak but a significant difference in the efficiency.

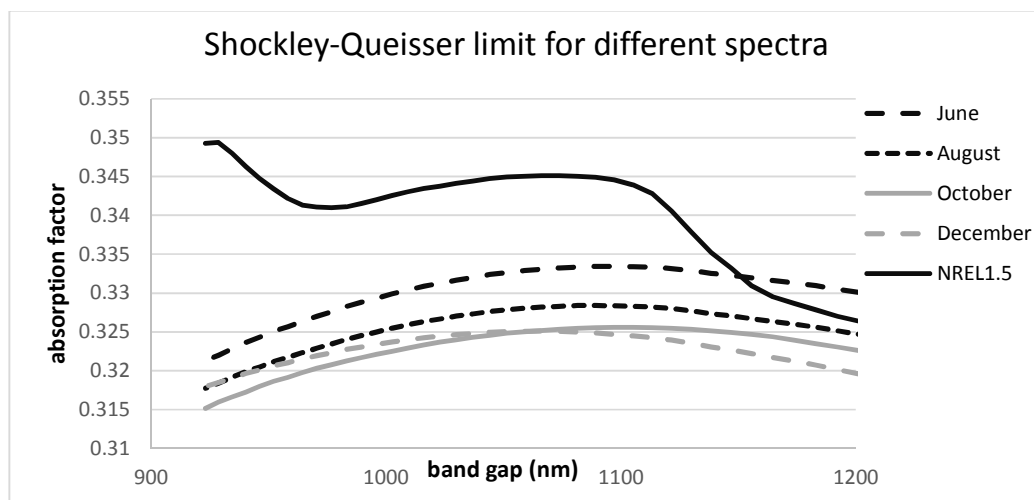


Figure 5: The Shockley-Queisser limit is compared between the months calculated for De Aar and that calculated for the NREL AM1.5 data.

5. Discussion and Conclusion

This study varies the band gap to investigate the effect the band gap has on efficiency and to find the optimal band gap for different spectra. The 925 nm band gap has been previously proposed [2] as the optimal band gap by applying the same approach done here to the NREL AM1.5 data. Figure 5 shows the peak for the limit calculated with the NREL AM1.5 data to be higher than those calculated for De Aar. This is due to the NREL AM1.5 data having more pronounced water vapour absorption bands, as these absorption bands are at higher wavelengths than the band gap, thus the energy absorbed is not affected but the total energy is lower which causes the absorption factor to be higher. In Figure 4 the effect of these water vapour absorption bands is visible at 07h30, the dip between 1400 nm and 1500 nm correlates with the water vapour absorption band that can also be seen at those wavelengths in Figure 1.

Since the radiative recombination depends on the number of electron-hole pairs, which in turn are dependent on the incident light, it is insufficient to use a single spectrum to estimate the yield for a day and hence it is argued that the approach adopted by us yields more accurate results.

It is evident that the optimal band gap for solar cells is not a single value for all scenarios as is often assumed [2, 3, 4], but rather dependent on the zenith angle and the makeup of the atmosphere. Figure 3 and 4 show the band gap with the highest efficiency vary from 1340 nm in the early morning to 1044 nm at mid-day respectively. For 21 June at De Aar under clear sky conditions, an ideal solar cell with the optimum band gap at 1089 nm gives a 33.34 % efficiency, while an ideal solar cell with band gap 925 nm gives 31.67 %. The deviation of the optimal band gap calculated here from the commonly adopted 925 nm [14] increases with zenith angle and thus at higher latitudes or during winter. Thus an ideal solar cell with band gap 1089 nm will yield 5.3 % more power than an ideal solar cell with the commonly accepted [14] optimal band gap of 925 nm over the conditions we investigated. The optimal band gaps for larger zenith angles (winter months and higher latitude) are closer to the band gap of typical mass produced photovoltaic cells (1107 nm for c-Si) [15] than the band gap suggested when calculating for the NREL AM1.5 data. It is then possible that solar cells with band gaps that are considered less desirable may be better suited to areas of high latitude or low precipitable water, or when maximum yield is desired in winter.

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Division G – Theoretical and Computational Physics

Hyperbolic extra-dimensions in particle physics and beyond

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Abstract. The nature of space-time at high energy is an open question and the link between extra-dimensional theories with the physics of the Standard Model can not be established in a unique way. The compactification path is not unique and supersymmetry breaking can be done in different ways. Compactifications based on hyperbolic orbifolds gather a large number of properties that are useful for this problem, like a Dirac spectrum chiral zero modes, a mass gap with the Kaluza-Klein modes, discrete residual symmetries for the stability of dark matter, and interesting cosmological constructions. This shall be explored here for bulk scalar fields, with a roadmap provided for fermionic studies and beyond.

1. Introduction

At the beginning of the twentieth century, the idea that spacetime could have more than four dimensions was put forward by Theodore Kaluza [1] and Oskar Klein [2]. What makes this idea of extra-dimensions so enduring is that they have not been ruled out by experiments, where we presume they are compact enough to have avoided detection thus far. In some scenarios they could even be large and still have avoided detection.

The idea of a large extra-dimensional model was first proposed by Arkani-Hamed, Dvali and Dimopoulos (ADD) [3, 4], where their ADD model introduced the idea that the Standard Model (SM) fields are confined to a brane (a four-dimensional manifold) which resides in the full spacetime. Due to their confinement to the brane, the SM fields do not feel the effects of the extra-dimensions, and experimental results are independent of their size. However, gravity is not so constrained given that it has no SM charges, and can feel the entire space. As such, large deviations from Newton's inverse square law are possible at short distances, though due to gravity being weaker than the other forces, this has only been experimentally verified to distances of the order of micrometres [5]. Therefore the limits placed on this gravitational law are very weak.

A primary motivation for studying extra-dimensional models was to resolve the hierarchy problem between the (effective) Planck scale, $M_{Pl} = \mathcal{O}(10^{18} GeV)$, and the electroweak scale, $M_{EW} = \mathcal{O}(100 GeV)$. This stems from the expectation that the bare Higgs mass would obtain corrections of the order of M_{Pl} , meaning some extreme fine-tuning of the Higgs sector parameters is required for the electroweak scale to be so low. The ADD model can solve this by virtue of the true Planck scale being related to the four dimensional Planck scale via the volume of the extra-dimensions. This is the result of gravity being able to propagate in the full spacetime, such that

the Planck scale we measure is effective and valid for energies smaller than the inverse radius of compactification of these extra-dimensions. As such, if the volume of the extra-dimensions is large enough, then the true scale of gravity can be as low as the electroweak scale. However, the ADD model's hierarchy problem resolution replaces the hierarchy between M_{EW} and M_{Pl} with another hierarchy, that between M_{EW} and the inverse radius of compactification for the extra-dimensions. Thus this ADD resolution only raises another question, why is the inverse radius of compactification so large when compared to the electroweak scale?

The construction of the ADD model assumes that the extra-dimensions are flat, with compactification being on a torus. But what if we change this assumption? Could other geometries for this space avoid this issue? Kaloper *et al.* [6], with this in mind, argued that a compact hyperbolic space may resolve this concern. At this point I note that other extra-dimensional models which contain branes do exist, for example the Randall-Sundrum model [7, 8] where two branes were used in its construction. We will not consider these models here, but note that experimental constraints on these models, from the search for Kaluza-Klein (KK) excitations of SM fields is highly dependent on which model you study. A range of models are currently studied at the Large Hadron Collider, for example see reference [9] from ATLAS and reference [10] from CMS.

In these proceedings we shall consider, as a preliminary step, the dynamics of a bulk scalar field in a hyperbolic extra-dimensional model and how to determine its KK spectrum. We shall then discuss possible extensions of this to fermion fields, and ultimately constructing a realistic model with all SM like fields and interactions.

2. Scalar Eigenmodes

As was discussed in the introduction, the ADD model resolved the hierarchy problem between M_{Pl} and M_{EW} by replacing it with a question as to why the radius of the extra-dimensional space is so large compared to the electroweak scale. If, however, the extra-dimensions were a hyperbolic disk with radius R , its volume would be:

$$V = \frac{4\pi}{\lambda^2} \sinh^2 \left(\frac{\lambda R}{2} \right) \sim \frac{\pi}{\lambda^2} e^{\lambda R}, \quad (1)$$

where λ is the constant negative curvature of our hyperbolic disk. This has the result that it is now possible to have $M_{Pl} \sim M_{EW} \sim R^{-1}$, that is, no new hierarchy is introduced if λ is of the order of the fundamental scale of gravity [11].

As there exist a range of possible hyperbolic geometries, we need to study which can provide us with the most interesting phenomenological features (to possibly provide dark matter candidates etc.). To begin this probe of possible spaces we look at scalar fields, where a great deal of information about the geometry of hyperbolic spaces can be obtained from the eigenmodes of the Laplace operator [12]. For hyperbolic spaces we have the Mostow-Prasad rigidity theorem [13] which ensures that different spaces have different eigenvalue spectra.

Note, though, that the eigenmodes of hyperbolic spaces cannot be expressed in a closed analytic form, as such numerical solutions are used. Of the numerical methods which exist the boundary element method of Aurich and Steiner [14] is the most powerful; however, here we shall use an alternative approach of Cornish and Spergel [12]. We appreciate that this method is technically weaker, but it is more adaptable to studying a variety of hyperbolic spaces as the only inputs are the group generators.

This approach is based on a grid over the extra-dimensional space, where we need a coordinate system on the hyperbolic space that allows us to make a discretisation in a sensible way. For example, a possible metric on a hyperbolic space, written in spherical coordinates, can be:

$$ds^2 = d\rho^2 + \sinh^2 \rho (d\theta^2 + \sin^2 \theta d\phi^2) . \quad (2)$$

In these coordinates the Laplace operator acting on a scalar field Φ is

$$\Delta\Phi = \frac{1}{\sinh^2 \rho} \left[\frac{\partial}{\partial \rho} \left(\sinh^2 \rho \frac{\partial \Phi}{\partial \rho} \right) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Phi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} \right]. \quad (3)$$

In the simply connected space the eigenvalues take all values in the range $q^2 = [1, \infty)$, and the eigenmodes are given by

$$Q_{q\ell m}(\rho, \theta, \phi) = X_q^\ell(\rho) Y_{\ell m}(\theta, \phi). \quad (4)$$

The $Y_{\ell m}$'s are spherical harmonics and the radial eigenfunctions are given by hyperspherical Bessel functions. The wavenumber, k , is related to the eigenvalues of the Laplacian by $k^2 = q^2 - 1$, and the modes have wavelength $2\pi/k$. These eigenmodes are also normalised.

As noted in reference [12], the eigenmodes can be lifted to the universal cover and expressed in terms of the eigenmodes of the hyperbolic plane, H^3 :

$$\Phi_q = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} a_{q\ell m} Q_{q\ell m}. \quad (5)$$

The modes Φ_q must satisfy the property

$$\Phi_q(x) = \Phi_q(gx) \quad \forall g \in \Gamma \text{ and } \forall x \in H^3, \quad (6)$$

in order to be a field on the hyperbolic plane with an orbifold, where Γ is the orbifold group. This places restrictions on the expansion coefficients $a_{q\ell m}$. As such, this equation can only be satisfied when q^2 is an eigenvalue of the compact space. To find these eigenmodes we solve the Laplace equation numerically. The rationale is that the wave equation has a set of solutions given by $\Phi(x, t) = \psi_q(x) e^{iqt}$, where ψ_q is an eigenfunction of Δ with eigenvalue $-q^2$. Provided the spectrum is discrete (the case for a compact space, where the size R of this space will also factor in the boundary conditions), the field has a Fourier transform in the time variable composed of Dirac peaks whose positions are given by the spectrum of the Laplace operator.

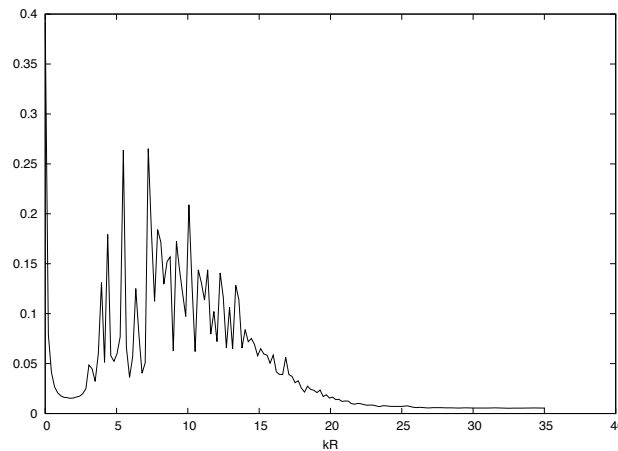


Figure 1. The KK spectrum for the illustrative example $m188(-1, 1)$ from *SnapPea*, where this is plotted in the range of the wavenumber, k , up to $kR = 35$.

As a test case we follow the example of reference [12] and choose from the *SnapPea* [15] census of closed hyperbolic 3-manifolds for the face-pairing generators $m188(-1, 1)$ (this is the name given in *SnapPea* and we use this for comparative purposes to the results given in reference [12]). We ran our code out to $kR = 35$ to produce the plot in figure 1. This figure shows an interesting feature common to these spaces, that of a zero mode followed by a mass gap, and then many modes after that which are nearly degenerate. Phenomenologically this could provide a wealth of dark matter states, which we are currently investigating further.

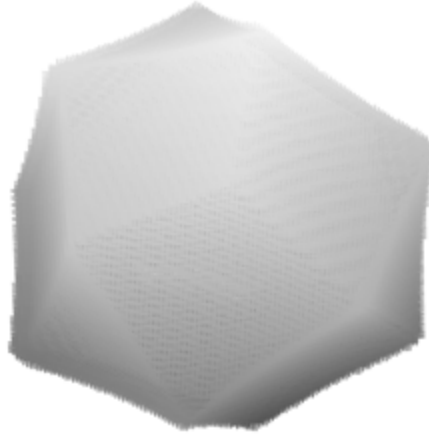


Figure 2. A Dirichlet domain for the space chosen above shown in Klein coordinates.

For those curious to see what the eigenmodes look like, we display in figure 2 a view of the Dirichlet domain, to help make contact with the 3-dimensional structure of the modes. Recall that the Dirichlet domain is the fundamental domain for lattices acting on curved spaces, see reference [13] and references therein for further details.

3. Future extensions

In order to now extend this to fermions in a bulk hyperbolic space, we first write the derivative part of the Dirac operator in Cartesian coordinates:

$$\not{\partial} = \sigma^a e_a^\mu \partial_\mu = \frac{1}{2} \left(1 - \frac{r^2}{L^2} \right) \begin{pmatrix} \partial_z & \partial_x - i\partial_y \\ \partial_x + i\partial_y & -\partial_z \end{pmatrix}. \quad (7)$$

We have here employed a nice compact (though not manifestly covariant) form for the dreibein

$$e_a^\mu = \frac{1}{2} \left(1 - \frac{r^2}{L^2} \right) \delta_a^\mu, \quad (8)$$

using our earlier example metric, equation (2), which gives the tangent frame

$$\Theta_\mu^a = \frac{2}{1 - r^2/L^2} \delta_\mu^a \quad (9)$$

and spin connection

$$\omega_\mu^{ij} = -x^{[i} \Theta_\mu^{j]} / L^2. \quad (10)$$

These shall be necessary for the construction of the appropriate Dirac equations, which we look forward to reporting on further soon.

Note, however, that a KK spectrum, as was observed in the scalar case, would be extremely interesting, phenomenologically, due to the possibility of chiral zero modes, as we know to be possible in six-dimensional theories [16]. Such chiral modes are not possible in five-dimensional theories, and many other extra-dimensional scenarios, but are crucial to the construction of the SM.

To conclude, the nature of space-time at high energy is an open question and the link between extra-dimensional theories with the physics of the SM can not be established in a unique way. The compactification path is not unique and in this proceeding we have sought to tackle this problem by starting from what is known from theory and experiment: the SM contains chiral fermions, the dark matter content of the universe and the difference between the electroweak and Planck scale should be explained. Compactifications based on hyperbolic orbifolds gather a large number of properties that are useful for these problems, like a Dirac spectrum chiral zero modes, a mass gap with the KK modes, discrete residual symmetries for the stability of dark matter, and interesting cosmological constructions [17, 18]. However, a complete model involving all SM-like fields is still to be constructed, where we hope to report on more progress along these lines at the next SAIP meeting.

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