

BAND MODEL OF DIFFUSION AND THE MEYER-NELDEL RULE

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In this article we present the band model of diffusion and consequently the explanation of the Meyer-Neldel rule (on its base) based on that.

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1. Introduction

1.1 Diffusion

Diffusion is a process proceeding on microscopic level and possessing a broad variety of forms. Diffuse molecules of: gasses, liquids, but also solids, diffuse constituent impurities inside ones. Diffuse carriers of electric charge – electrons, holes and ions. Diffusion affects particulate processes on molecular level – chemical reactions catalyze even phase transitions of different types [1-12].

Important role diffusion plays in solids [9-12]. Numerous micro-structural changes and numerous chemical reactions in solid state take place through solid state diffusion, i.e. the movement and transport of atoms in solid phase. The diffusion takes place because of the presence of defects in solids. Point defects, e.g. vacancies and interstitial ions, are responsible for lattice diffusion. Diffusion also takes place along line and surface defects which include grain boundaries, dislocations, inner and outer surface, etc.

The diffusion of atoms in solids represents a large number of jumps per unit time and the distance that each particle moves in each jump. One important quantity by describing diffusion is diffusion coefficient, which represents the proportionality constant between the particle flux and the concentration gradient. That relation represents mathematically the Fick's first law [1,2]. In numerous practical cases the concentration and gradient of concentration changes with time. Such cases are covered by Fick's second law [1,2].

In the literature on diffusion and diffusion-controlled reactions or processes one encounters many different terms that describe the diffusion behavior under different experimental conditions: tracer and self-diffusion of atoms and ions, diffusion of defects, chemical diffusion, ambipolar diffusion, a.o. [1-12].

Diffusion rates may, in principle, be determined from any property or reaction which depends on atomic mobility. By way of illustration, in ionic conductivity of the anion is directly proportional to the anion diffusion coefficient. The use of isotopes or tracers is a common means of studying diffusion. Tracer methods permit measurements of self-diffusion, that is, the diffusion of the crystal components in a crystal. In the case of defect clusters it has alternatively been proposed that the smaller clusters may move as a unit.

Diffusion often takes the form of an excitation characterized with some activation energy [13-30]. Grain boundary and dislocation diffusion generally have smaller activation energies than lattice diffusion. Activation character appears itself chiefly by influence of temperature on diffusion process. Just, this fact induced us to propose a band model of diffusion. A strong support for that model offered chiefly a possibility to explain - based on it - Meyer-Neldel empirical rule.

This will be explained later in this article. The MNR describes development of many diffusion processes as well as ones closely connected with diffusion.

Many attempts have been made to explain the MNR (compensation effect) for various processes. It must be concluded, that despite there is still no broadly accepted explanation [13-31].

Further, the band model of diffusion will be characterized and later on the explanation of MNR for diffusion processes will be submitted. In conclusion some remarks will be introduced concerning possibility of explanation of validity MNR in catalytic chemical processes and in phase transitions, too.

1.2 The Meyer-Neldel rule (MNR)

The MN empirical rule was discovered by Meyer and Neldel in 1937 at investigation of electrical conductivity some semiconducting substances [22]. Semiconductors are characterized by the temperature dependence of their electrical conductivity. Most semiconductors exhibit an exponential temperature dependence of the conductivity, $\sigma(T)$

$$\sigma = \sigma_0 \exp\left(-\frac{W}{kT}\right) \quad (1)$$

where σ_0 is a constant and W – activation energy [9-12, 32-37].

If the logarithm of the conductivity σ is plotted on the ordinate against the reciprocal of the temperature T on the abscissa, a straight line is obtained whose slope one may calculate the activation energy, W . The extrapolated intercept of this line on the ordinate axis yields the value of the pre-exponential factor, σ_0 .

For many classes of materials, especially organic semi-insulators, chalcogenide glasses, amorphous silicon...experimental evidence suggest that a correlation exists between the activation energies and pre-exponential factors of the following form [13-31].

$$\ln \sigma_0 = bW + \ln \sigma_{00} \quad (2)$$

where b and σ_{00} are constant. This relation can be written as

$$\sigma_0 = \sigma_{00} \exp\left(\frac{W}{kT_0}\right) \quad (3)$$

here $b = 1/kT_0$. The relation (3) gives the dependence of pre-factor σ_0 on the activation energy W and represents Meyer-Neldel empirical rule. Equation (3) is often referred to as the MN rule or the compensation rule. Constant σ_{00} is often called the Meyer-Nedel pre-exponential factor and kT_0 the MN characteristic energy.

The MNR is in fact a special case of so called compensative effect [7], which was discovered by Wilson [31] in 1908. Since the discovery of a compensative effect for the electrical conduction in TiO_2 , Fe_2O_3 , by Meyer and Neldel in 1937, the linear compensative effect has often been referred to as the Meyer-Neldel rule, especially in relation to conductivity and diffusion phenomena.

The MNR is generally observed in disordered materials. In the class of amorphous semiconductors, the MNR has been reported for a-Si:H films in which W is varied by doping, by surface absorption, light soaking or by preparing films under different conditions. This rule has also been observed for liquid semiconductors and fullerenes. The validity of MNR has been reported in the chalcogenide glasses. However, in case of these glasses this rule is observed by the variation of activation energy W on changing the composition of the glassy alloys in a specific glassy system.

In works [16-18] the change of activation energy W was caused under influence of an electric field or a light. Up to now there is not the generally accepted theory explaining the MN rule satisfyingly.

1.3 Explanation of the MNR at electrical conductivity of semiconductors

Basic ideas concerning the MNR explanation in a case of electrical conductivity in non-crystalline semiconductors, namely, in chalcogenide glasses, non-crystalline silicon, Si and Si:H were presented in work [38]. The explanation is based on the barrier-cluster model of a non-crystalline semiconductor [38]. Validity of the Meyer-Neldel rule in non-crystalline semiconductors can be explained assuming that recombination transition of an electron from conduction band to valence band is conditioned by emission of number monoenergetical phonons which total energy corresponds to the width of forbidden band (and so to the energy extracted in transition). Probability of such complex process is determined by number of emitted phonons. This probability exponentially decreases with increasing number of phonons and consequently with width of the forbidden band. The probability of recombination influences equilibrium concentration of free electrons in conduction band and subsequently electric conductivity. In such a way we have finally obtained the relation which is equivalent to the Meyer-Neldel rule [38].

2. The band model of diffusion and the MNR explanation

2.1 Basic relations

Observations show that the diffusion often has excitation (activation) character. This is expressed by activation dependence of diffusion coefficient D on temperature T in a form

$$D = D_0 \exp\left(-\frac{W}{kT}\right) \quad (4)$$

where W is the activation energy of a diffusion process and D_0 je pre-exponential factor. This relation resembles to the relation (1) for electrical conductivity. In a case of diffusion in corresponding formulae instead of electrical conductivity of a semiconductor emerges the diffusion coefficient D .

If the MNR is valid then for diffusion pre-exponential factor D_0 holds

$$D_0 = D_{00} \exp\left(\frac{W}{kT_0}\right) \quad (5)$$

where D_{00} and T_0 are constants. The relation (5) is analogy of the relation (3).

For diffusion coefficient of upper mentioned group of substances it holds

$$D = D_{00} \exp\left(\frac{W}{kT_0}\right) \exp\left(-\frac{W}{kT}\right) \quad (6)$$

2.2 Band model for impurity diffusion

To description of activation processes shows to be suitable the band model like that one, which is successfully used for description of electric properties of semiconductors. One typical feature of that model is existence of forbidden energy gap separating a valence band from a conduction band. The band model prepared the way for explanation and validity of the MNR at electrical conductivity non-crystalline semiconductors [38]. Analogical band approach, likely, is suitable for description of diffusion processes in solids and liquids. The fundamentals of this

model will be described later.

The band model of particle diffusion – e.g. impurity atoms in a non-crystalline substance, assumes that impurity atoms of a diffusing matter are to be found at low energies in the ground (basic) band therefore in the band of low (nearly zero) mobility. In this simplifying model we shall consider mobility of these particles in the ground (basic) band to be zero. At sufficiently enough energy the particles (atoms) of the ground band can be excited over the forbidden band into the band of non-zero mobility. The atoms need sufficiently enough to this transition. This process is called activation one.

The concentration n of impurity atoms in the band of non-zero mobility will be determined by the relation

$$n = n_o \exp(-W/kT) \quad (7)$$

This concentration is closely connected with the coefficient of diffusion D . The proportionality $D \approx n$, will hold, so that

$$D = D_o \exp(-W/kT) \quad (8)$$

Experiments with diffusion showed that quantities n_o a D_o at the changes of activation energy W change in dependence on it according to so called empirical Meyer-Neldel rule, namely as

$$n_o = n_{oo} \exp(W/kT_o)$$

resp.

$$D_o = D_{oo} \exp(W/kT_o) \quad (9)$$

where n_{oo} , D_{oo} and T_o are constants.

Next, will be shown that Meyer-Neldel dependence (9) can be explained under specific conditions connected with transition of excited atoms from the diffusion band (from a state of non-zero mobility) to the ground – non active band (of zero mobility).

2.3 Dependence of diffusivity D on activation energy W

Our model assumes that there are not energy levels of significant concentration in forbidden band. Conditions of the MNR validity in a given diffusion process are connected with transition of an atom from the diffusion band into the ground band.

A transition of an atom from diffusion band to basic band in disordered materials proceeds predominantly by production of phonons. The total energy of produced phonons will correspond to that one released in atom transition. It is going on energy corresponding to the forbidden band width equal to $2W$. Further, we shall assume that in a substance under consideration dominates phonon production which average energy is ΔE . It means, that phonon production of other phonons is negligible. At the transition of an atom from diffusion band to basic band gained energy $2W$ is used in production of N phonons each of them has energy ΔE so that $2W = N\Delta E$ or

$$N = 2W/\Delta E \quad (10)$$

Let w_1 be probability of production one phonon which energy is equal to ΔE . Probability w_N of production N phonons of equal energy due to the excited atom – lattice interaction will be

$$w_N = (w_1)^N \quad (11)$$

If we write down probability w_1 as

$$w_1 = \exp(-\varepsilon_1) \quad (12)$$

where ε_1 is a positive value, then probability w_N one can write with respect to (10-13) as

$$w_N = \exp(-N\varepsilon_1) = \exp(-\varepsilon_1 2W/\Delta E) = \exp(-bW) \quad (13)$$

where the constant b is given by

$$b = 2 \varepsilon_1/\Delta E \quad (14)$$

Relation (13) gives at the same time the transition probability of an atom from diffusion to basic band. That one is proportional to the probability of production N phonons and thus proportional to the $\exp(-bW)$. With an increase of activation energy W , the probability of the transition of atom in to basic band according to (13) exponentially decreases.

2.4 Equilibrium concentration of excited particles

An equilibrium concentration n of excited atoms occurring in the diffusion band is a result of two opposite processes: one is a process of generation and the other one is a process of „annihilation of free atoms“ in diffusion band. In equilibrium (or steady) state it holds

$$(dn/dt)_{\text{gen}} = (dn/dt)_{\text{recom}} \quad (15)$$

We shall assume, that a number n of excited particles generated in a unit time is given as

$$(dn/dt)_{\text{gen}} = G = C_1 \exp(-W/kT) \quad (16)$$

where C_1 is a constant.

For an „annihilation“ process we suppose that the relation

$$(dn/dt)_{\text{recom}} = R = n.C_2 \exp(-bW) \quad (17)$$

is valid. Here C_2 is a constant. The number of annihilation in a unit of time is proportional to the number n . In equilibrium state it valid $R = G$, so that

$$C_1 \exp(-W/kT) = n.C_2 \exp(-bW) \quad (18)$$

From that relation follows for equilibrium concentration n of free atoms

$$= C_{00} \exp(bW) \exp(-W/kT) \quad (19)$$

where C_{00} is determined by the constants C_1 and C_2 .

2.5 Diffusivity coefficient

It is known that diffusivity coefficient D is proportional to n : $D \approx n$. If mobility of free particles in diffusion band is independent on activation energy W (or that dependence is negligible) one can write with respect to (19)

$$D = D_{00} \exp(bW) \exp(-W/kT) \quad (20)$$

respectively

$$D = D_0(W) \exp(-W/kT) \quad (21)$$

where D_{00} is a constant and

$$D_0(W) = D_{00} \exp(bW) \quad (22)$$

If we put $b = 1/kT_0$, the relation (21) takes the form which is identical with dependence (6)

$$D \approx D_{oo} \exp(W/kT_o) \exp(-W/kT) \quad (23)$$

The relation (22) acquires the form

$$D_o \approx D_{oo} \exp(W/kT_o) \quad (24)$$

which expresses the Meyer-Neldel rule (9) for diffusion.

2.6 Physical foundation of the diffusion band model

The best arguments in favor of presented hypothesis concerning band model of diffusion one can seek in physics of semiconductors. Just there has been for the first time elaborated and theoretical well-founded band theory of electrical conductivity of semiconductors. It has been resulted from solution of the problem of an electron motion in periodic (electric) field of a crystal. If one replaces electron by other particle – say, by diffusing impurity atom – then analogical situation arises. Diffusing atom also is moving in a periodic force field of an atomic lattice. Moving atom is a particle which motion complies with laws of quantum mechanics. The difference consists in that; the atom has greater mass then electron. It does not change the essence of our analogy.

In a case of diffusion it is unsuitable to speak about recombination which is used at semiconductors. That is not significant for creation of a band structure.

The band model of diffusion well fits activation character of diffusion and also the MNR for diffusion, as it was shown in preceding section. Moreover, the band model of diffusion enables to understand activation character and validity of the MNR at catalysis and others chemical processes and at phase transitions, too.

The Meyer-Neldel rule can not be connected with anyone diffusion in a solid. Sometime, the Arrhenius relation with constant pre-exponential factor can be valid. The MNR will present such a diffusion at which the transition from diffuse band into ground band over forbidden band is realized with emission a number of phonons of relative low energies (compare to the width of energy gap).

Transfer of particles in a substance proceeds mainly in diffusion band. It is connected with varied scattering mechanisms in dependence on sort of material. Of course, materials in which dispersion takes place have average value of diffuse mobility significantly lower - due to the scattering, than in crystals. Some sort of short distance periodicity exists, too, due to the short distance ordering of atoms in non-crystalline materials with dispersion.

3. Discussion

3.1 The MNR at catalysis

Activation mechanism –as it is known - takes place also in catalytic processes [43-45]. It seems to us, that the diffusion is responsible therefore. Probably, the MNR dependence observed in catalytic processes is connected with that mechanism. Catalysis is tightly connected with diffusion at a surface or other type of diffusion. Next, as an illustration we shall introduce a simplifying model of one sort of catalysis.

Let us assume, that at catalytic synthesis of atoms of a type A with atoms of a type B; it means at catalytic reaction



it is in progress as follows:

Atom A is caught at the surface of a metallic (catalyst) catalyzer (e.g. platinum) at the fixed position. Atom B is also caught at the surface of a metallic catalyzer but it will be able to diffuse at the surface of the catalyzer. In fact, it will be proceed - according with concept upper

described band model – in such a way that atom B will be in a state of zero mobility or in an excited state of non-zero mobility. Its activation energy will be W_B and it will participate in surface diffusion. Excited atom B can self energy submit through multiple creation of phonons comparatively low energy in comparison with energy W_B . That process creates suitable conditions in which the MNR is valid i. e. not only for surface diffusion of a particular atom B at the surface of a catalyzer, but also for all long chain of such actions – catalytic process.

The catalytic chemical reaction – as it is believed – will be realized when diffusing atom B comes close enough to the fixed atom A. When catalytic reaction – in which participates the catalyzer, too – will be over, resulting molecule AB will be free. It is the product of catalysis. The number of AB will be proportional to the number of atoms B in the excited state, because only these atoms can participate in catalytic fusion with atoms A.

Just, above described process of catalysis will be conditioned by surface diffusion at least one type of atoms. Catalysis will show activation character, because such character has one link of a chain of actions. The MNR will be valid for catalysis, too.

Analogical activation process can be connected with diffusion of A at the surface of a catalyst. If the activation energy W_A is much greater then the activation energy W_B the process of one type will predominate only, as a result.

3.2 The MNR at phase transitions

Diffusion plays an important role at phase transitions, too [43-45]. It can represent one intermediate (interface) in a process of phase transformation. Diffusion can significantly contribute to the particle transfer between phases. If it is true, then an activation process affecting diffusion is at the same time an activation process of whole phase transition. It results to the validity MNR at phase transition.

3.3 Remarks

It seems to us, that the MNR is fulfilled always, when the band model - in which participates the forbidden energy band - is applicable on such a process. Activation of a particle is realized – with concept of model described above – via transition over forbidden band. Moreover, a condition of validity the MNR is submission energy by a particle passing down via forbidden band to the creation multiple emissions of phonon relatively low energy.

Likely, these conditions are well fulfilled in disordered structures, in non-crystalline semiconductors and at diffusion processes in liquids. These processes secondary affect catalysis and phase transitions and obviously also others, mainly chemical processes in substances.

The problem of explanation MNR observed at electron emission from metal (platinum) into hydrogen by Wilson [31] in 1908 stays still open. But also in this case is not excluded an attendance at surface diffusion, namely of hydrogen, at emission process of electrons from metal. Such diffusion should result into fulfillment of the MNR.

4. Conclusions

The band model of diffusion is an analogy of the energy spectrum of an electron in semiconductors with typical valence band, conduction band and forbidden band (or energy gap) in between. At diffusion the energy levels does not belong to an electron but to a diffusing particle e.g. atom. To the conduction band of a semiconductor corresponds a diffuse band of non-zero mobility of particles. The ground (basic) band, non-active band of nearly zero mobility, corresponds to the valence band of a semiconductor. Energies inside the forbidden band are forbidden for particles (atoms).

The band model well fits the activation character of diffusion. In addition, it permits to explain the validity of the MNR at diffuse processes, under the assumption of multiple phonon transition of a particle from the band of high diffuse mobility to the band of zero diffuse mobility. At certain low energies emitted phonons such transition requires emitting of a great number of

phonons. The broader the forbidden band is, the greater number of phonons has been emitted at transition. Thus, the transition probability decreases.

Transition probability exponentially decreases with increase of forbidden band width (or activation energy). That leads to an increase of impurity atom concentration in the diffuse band of high mobility. Just, this is the source of dependency pre-exponential factor on activation energy. The validity of the MNR at diffusion is transferred on further physical processes affected by diffusion. Here belong: catalysis, phase transitions and many chemical processes.

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References

- [1] P.G. Shewmon, Diffusion in solids, McGraw-Hill, New York, (1963).
- [2] J. Philibert, Atom movements. Diffusion and mass transport in solids, (S.J. Rothman, Engl. Transl.) Les Editions de Physique, Les Ulis. (1991).
- [3] I. Kaur, Yu.Mishin, W.Gust, Fundamentals of grain and intephase Boundaryh Diffusion, John Wiley&Sons, Chichester, (1995).
- [4] G. Antezak, G. Ehrlich, Suface Science Reports **62**, p. 39-61, (2007).
- [5] J. Crank, The matematics of Diffusion, 2nd. Ed. Oxford Science Publ., Oxford , (1975).
- [6] K. Oura, V.G.Lifshits, A.A.Saranin, A.V.Zotov, M.Katayama, Suphace Science: An interoduction, Springer-Verlag Berlin , Heidelberg, ISBN 3-540-005-45-5, (1963).
- [7] D. Fisher, Defect and diffusion forum volumes 192-193, (1994-1997).
- [8] J.C. Fisher, J.Appl. Phys. **22**, 74, (1951).
- [9] N.F. Mott, E. A. Davis, Electron processes in non-crystalline materials, Clarendon Press, Oxford 1979. (Elektronnyje processy v nekristaličeskich veščestvach, Mir, Moskva 1982).
- [10] M.H. Brodsky, Amorphous semiconductors, Springer Verlag Berlin, Heidelberg - New York 1979. (Amorfnyje poluprovodniky, Mir, Moskva 1982).
- [11] M.A. Popescu, Non-crystalline chalcogenides, Solid state science and technology Library, Vol.8, Kluwer academic publishers, Dordrecht/Boston/London (2000).
- [12] M. Popescu, Physics and Applications of Disordered Materials, INOE Publishing House, (2002).
- [13] R.S. Sharma, N.Mehta, A.Kumar: Chin.Phys. Lett. **25**(11), 4079 (2008).
- [14] H. Schmidt, M. Wiebe, B.Dittes, M.Grundmann, Annual report IIM 2007, FZD – 493 Applied physics letters **91**(232110), 37 (2007).
- [15] N. Kushwaha, N.Mehta, R.K.Shukla, D.Kumar, A.Kumar, Journ. of Optoelectr. and Adv. Mater. **7**(5), 2293 (2005).
- [16] D. Kumar, S.Kumar, Turk J.Phys 29, 91, (2005).
- [17] D. Kumar, S.Kumar, Journ. of Optoelectr. and Adv. Mater., **6**, p.777, (2004).
- [18] D. Kumar, S.Kumar, Chalcogenidel letters **16**(6), 79 (2004).
- [19] R. Widenhorn, M. Fitzgibbons, E. Bodegom, Journ. of applied physics **96**(12), 7379 (2004).
- [20] N. Mehta, D.Kumar, A.Kumar, Journal of physical studies **9**(3), 238, (2005).
- [21] R.S. Crandall, Physical review B **66**, 195210-1 - 195210-8, (2003).
- [22] W. Meyer, H.Neldel, Z. Tech. Phys. (Leipzig), **18**, 588 (1937).
- [23] K. Shimakawa, F.Abdel-Wahab, Appl. Phys. Lett. **70**, 652, (1997).
- [24] M.L. Zhang, S.S. Zhang, E. Pollak, J.Chem. Phys. **119**, 11864, (2003).
- [25] A.Yelon , B.Movaghar, R.S. Crandall, Rept. Prog. Phys. **69**, 1145, (2006).
- [26] Abd-El Mongy A Physica B **305**, 259, (2001).
- [27] S.R. Elliot Philos. Mag. B **36**, 1291, (1977).
- [28] P.Nagel, H.Ticha, L. Tichy, A. Triska, J. Non-Cryst. Solids, **50-60**, 1015, (1983).

- [29] J.C. Philips, *J. Non-Cryst. Solids*, **43**, 37 (1981).
- [30] T.A. Abtew, MingLiang Zhang, Yue Pan, D.A.Drabold: *Journ. Non-Cryst. Solids*, **354**, 2909 (2008).
- [31] H.A. Wilson, *Philos. Trans. A*, **208**, 247, (1908).
- [32] A. M. Andriesh, M. S. Iovu, S. D. Shutov, *J. of Optoelectr. and Adv. Mater.* **4**, 3 (2002).
- [33] M. Andriesh, M. S. Iovu, *Moldavian journal of physical science*, **2**(3-4), 246 (2003).
- [34] *Non-Crystalline Materials for Optoelectronics, Series: Optoelectronic Materials and Devices, Vol. 1*, June 2004, Editors: G. Lucovsky, M. Popescu, INOE Publishing House, 2004, 482 pp. (Hardbound) ISBN: 973-85818-0-X ; ISSN: 1584-5508, (2004).
- [35] M. Popescu, *Journ. Optoelectron. Adv. Mater.* **6**(4), 1147 (2004).
- [36] M. Popescu, F. Sava, A. Lorinczi, *Chalcogenide Letters* **1**(9), 111 (2004).
- [37] *Advances in Amorphous Semiconductors (Volume in the Series "Advances in Condensed Matter")* Authors: Jai Singh, Koichi Shimakawa, Gordon & Breach/Taylor & Francis, London, April 2003, 336 pp., ISBN 041528707, (2003).
- [38] I. Banik, *Chalcogenide Letters*, **6**(12), 629 (2009).
- [39] I. Banik, *Central Europ. Journ. of Physics*, **3**(2), 270 (2005).
- [40] I. Banik, *Journ. Non-Cryst. Solids*, **353**, 1920 (2007).
- [41] I. Banik, *Journ. of Optoelectr. and Adv. Mater.* **11**(12), 1915 (2009).
- [42] I. Banik, *Journ. of Optoelectr. and Adv. Mater.* **11**(12), 1931 (2009).
- [43] T. Bligaard, K.Honkala, A.Logadottir, J.K.Norskov, S.Dahl, C.J.H.Jacobsen, *J.Phys.Chem. B.* **107**, 93235 (2003).
- [44] E. Shustorovich, *Metal-surphace Reaction Energetics: Theory and applications to Heterogeneous Catalysis, Chemisorption and Surphace Diffusion*, VCH Publishers, Inc. ISBN 3-527-27938-5, (1991).
- [45] N. Mehta, A.Kumar, *Journ.of Physical Studies*, **10**(2), 117 (2006),