



Synthesis and characterization of Mn doped ZnS pellets

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Abstract

Semiconducting nano-phosphor pellets have been fabricated by hydraulic pressure, using ZnS and Mn doped ZnS semiconducting materials, which is synthesized by physical evaporation technique. Structural characterizations of synthesized semiconducting nanophosphor materials and pellets have been done by X-ray diffraction measurement and SEM while optical characterizations are done by UV-Visible absorption measurement. XRD pattern showed that the synthesized ZnS, Mn doped ZnS materials and pellet have cubic structure with preferential orientation along (111) planes. Optical absorption measurements indicated that the absorption decreases with increase of percent of Mn in pellet. The average maximum grain size (25.13 nm), Minimum dislocation density ($1.57 \times 10^{11}/\text{cm}^3$), lattice constant (5.398 Å) and minimum band gap (3.2 eV) have been obtained. Suitable explanation is given in this paper.

Keywords: ZNS, MN, Grain Size, Band Gap and Lattice Constant.

1. Introduction

In recent years, semiconducting nanophosphor materials have found wide application in nano-science and nano-technology due to its unique physical and chemical properties, such as quantum size effects [1], [2], abnormal luminescence phenomenon [3]. Nano-semiconductor is back bone of optoelectronic devices. Nanophosphor ZnS semiconductor exists in two phases, i.e. cubic phase and hexagonal phase because crystal structure changes with grain size of the particle. Zinc sulphide belongs to II-VI compound semiconductor with wide direct energy band gap of 3.68-3.91 eV at room temperature. It has high refractive index (2.25), melting point (2038 K), lattice constant (5.4104 Å) and wide wavelength pass band (0.4 -13 μm) [4]. Nanomaterial ZnS has been used in many optical devices such as ultraviolet light-emitting diodes [5], [6], flat panel display [7] and thin film electroluminescence [8,9]. ZnS also applied in luminescent materials which have generally zinc blende structure [10]. ZnS nanostructures have been prepared in different form due to their potential applications such as ZnS nanorods [11], nanowires [12], nanotubes [13] and nanobelts [14] etc but in pellet form is not described in wide range. Several synthesis methods such as solvothermal decomposition [15], microwave synthesis [16], solution route [17], colloidal synthesis [18], pyrolysis in furnace [19] and hydrothermal method [20], have been used but physical method is not used for preparation of these materials. In this paper we synthesis the Mn doped ZnS by physical method and prepare pellet by hydraulic pressure because this is inexpensive technique and fast technique for growing thick films/pellet. Here we studied the effect of Mn doping percent on the structural and optical properties of ZnS pellets.

2. Experimental

2.1. Chemicals

For the preparation of Mn-doped ZnS nano-material and pellets, the materials are used zinc sulphate [M=288] and manganese [M=169.6]. All chemicals were purchased from Alfa Aesar, Ltd. USA, which have high purity 99.99%.

2.2. Synthesis of materials

Mn doped zinc sulphide materials are synthesized by physical evaporation method. Zinc sulphate and manganese are used as reactant materials. Freshly, weighing certain amount of ZnS and Mn for preparation of different sample of ZnS:Mn using Sartorius chemical balance in Department of Microbiology, Dr. R M L Avadh University, Faizabad. Initially mixed ZnS and 2% percentage Mn and grinded by mortar rod for preparation of homogeneous materials. Prepared materials put into molybdenum boat and heated in vacuum coating unit (Model 12 A4) under vacuum 10^{-3} - 10^{-4} Torr for five hours for solid powder reactions. This process was repeated 3 times for solid powder reactions for same sample. This process was repeated for other sample (3 % Mn in ZnS).

2.3. Preparation of pellets

Undoped zinc Sulphide and manganese doped zinc sulphide pellets have been fabricated by hydraulic pressure (upto 10 Tonn) using thermally synthesized nano-materials of ZnS in Department of Physics, Lucknow University, Lucknow.

3. Characterization

3.1. Structural characterization of Nano-materials and its pellets

The X-ray Diffraction (XRD) patterns of nano-materials and pellet of ZnS with Mn doped and undoped are recorded by Rigaku diffractometer using graphite filtered $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54 \text{ \AA}$) at 40 KV, 100 mA with a scanning rate of 3 degree per minute (from $2\theta = 20^\circ$ to 60°) in Department of Physics & Electronics, Dr. R M L Avadh University Faizabad. The crystallite sizes and dislocation density of ZnS and ZnS:Mn are calculated by using Debye Scherrer's formula[21].

$$D = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

$$\text{Dislocation density} = \frac{1}{D^2} \quad (2)$$

Where λ is wavelength of radiation used, θ is diffraction angle of the concern diffraction peak, β is the full width at half maximum (FWHM) of the diffraction peak corresponding to a particular crystal plane.

Scanning electron micrograph of undoped and Mn doped ZnS nanomaterials/pellets also have been recorded in department of Physics & Electronics, Dr. R M L Avadh University, Faizabad,U.P (India)

3.2. Optical characterization

Optical absorption spectra for undoped and doped ZnS (Mn doped in ZnS) pellets are recorded by a Shimadzu double beam double monochromator spectrophotometer (UV-2550) in the wavelength range 200 - 600 nm.

4. Result and discussion

4.1. Structural properties of nanomaterial's and its pellet

X-ray diffraction patterns of undoped ZnS and Mn doped ZnS nanomaterials and pellets are shown in Fig.1&2. The XRD measurement reveals that the nanocrystalline of ZnS and ZnS: Mn has cubic structure. Nanocrystals have different plane (111), (200), (220) and (311) with preference orientation along (111) plane. The cubic phase of the crystals was identified from the agreement of peak position with standard JCPDS data card no. 65-1691. Experimental and standard d value of ZnS nanomaterials are given in Table-1.

The grain size of crystal calculated using scherrer formula and given in Table-2. The grain size increases with increase of doping percent of Mn in starting nanomaterial and pellet. Grain size is much better in pellets than the nanomaterials of ZnS. This may be due to collapse of nano-particle each other and decrease crystal defects in pellets. Maximum grain size 25.18 nm have been obtained. The lattice constant and dislocation density of this material also calculated which are also given in Table.2. Dislocation density decreases with increase of doping of Mn percentage and minimum dislocation $1.57 \times 10^{11}/\text{cm}^3$ have been obtained. The obtained grain size, lattice constant and dislocation density of pellets and nano-materials in present investigation are similar with other investigators [22], [23].

Table 1: Experimental and Standard D Value

S.No	(hkl) plane	Experimental d value ($\text{\AA}$)	Standard d value($\text{\AA}$)
1	111	3.117	3.123
2	220	1.912	1.912
3	311	1.629	1.633

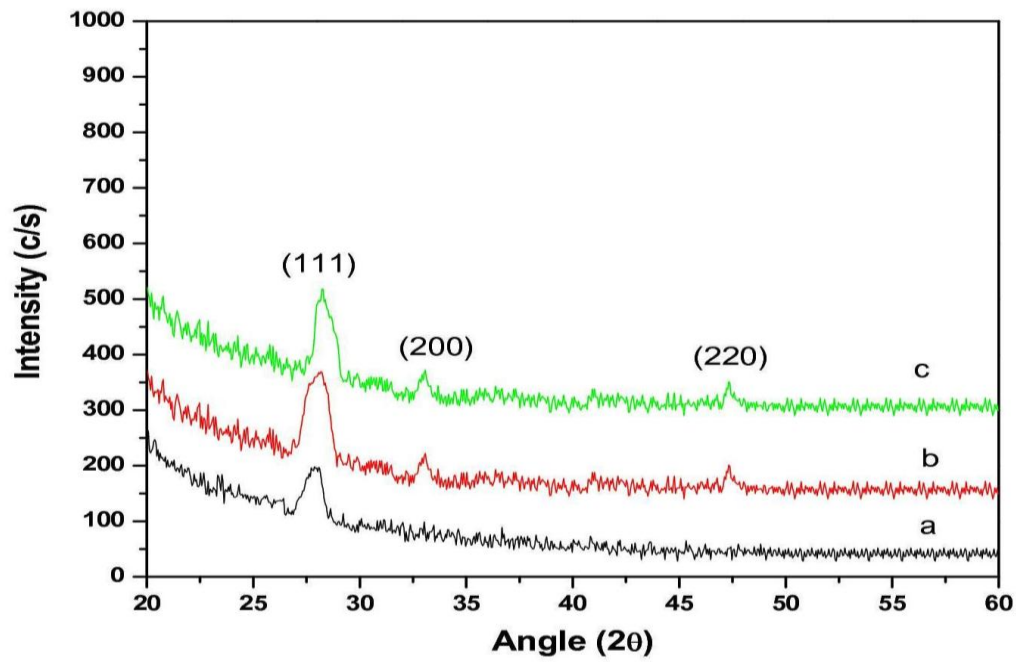


Fig. 1: XRD Pattern of Nanomaterial's (A) ZnS (B) ZnS: 2% Mn (C) ZnS:3%Mn

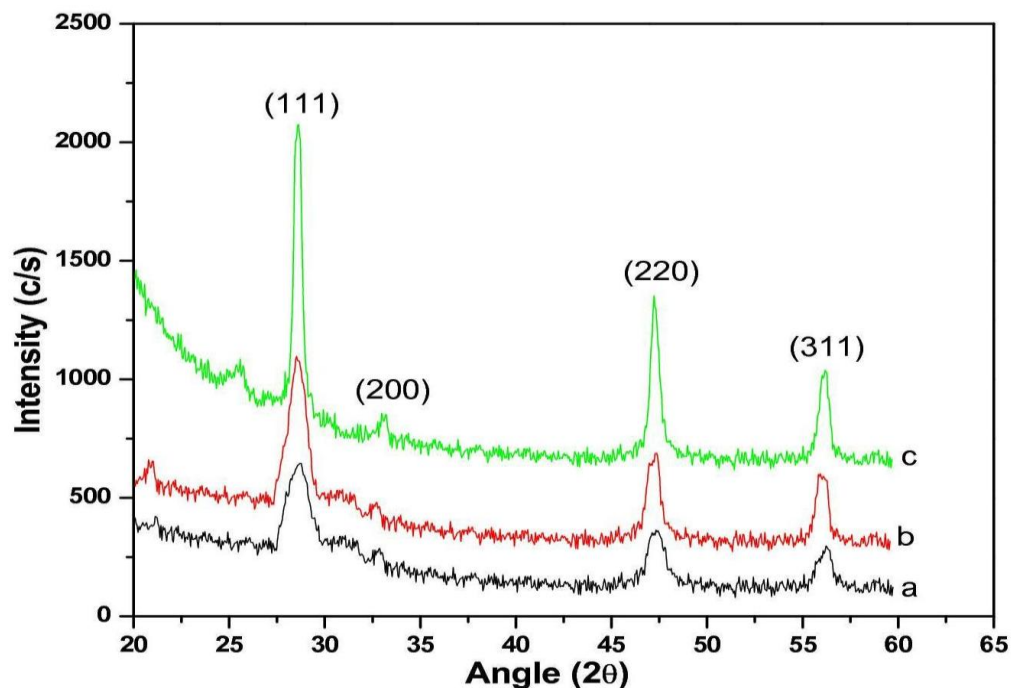


Fig. 2: XRD Pattern of Pellets (A) ZnS (B) ZnS: 2% Mn (C) ZnS:3%Mn

Table 2: Structural and Optical Parameters

S.No	Sample	Nanomaterials (Powder)			Pellets			Band gap (eV)
		Grain size (nm)	Dislocation density $\times 10^{11}/\text{cm}^3$	Lattice constant($\text{\AA}$)	Grain size(nm)	Dislocation density $\times 10^{11}/\text{cm}^3$	Lattice constant($\text{\AA}$)	
1	ZnS	11.23	7.93	5.389	15.25	4.29	5.399	3.5
2	ZnS: 2 %Mn	13.33	5.62	5.411	19.23	2.70	5.401	3.4
3	ZnS: 3% Mn	14.76	4.59	5.261	25.18	1.57	5.362	3.3

4.2. Scanning electron microscopy characterization

The surface morphology of undoped and Mn doped ZnS pellets which fabricated by hydraulic pressure, are shown in Fig.3. It is clear from Fig.3 that the fabricated pellets are homogenous, without crack and pin holes. This is good agreement with X-ray diffraction of Mn doped ZnS pellets.

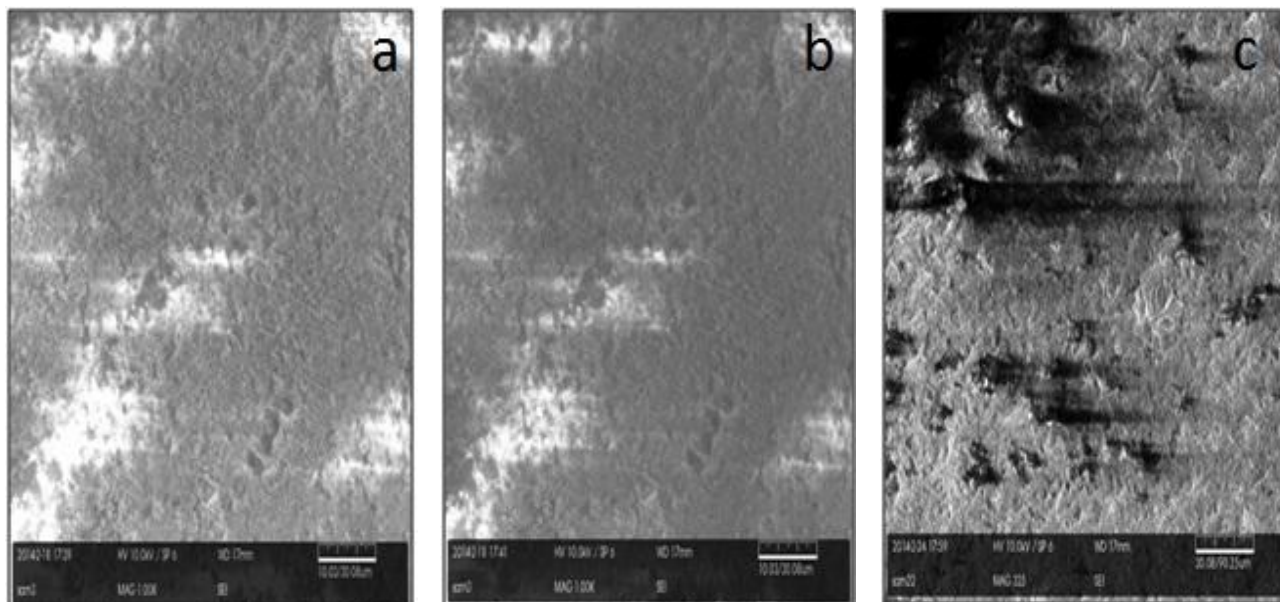


Fig. 3: Scanning Electron Micrograph of Undoped and Doped ZnS Nanocrystals (A) Undoped ZnS Pellet (B) 2 % Mn Doped ZnS Pellet (C) 3 % Mn Doped ZnS Pellet.

4.3. Optical properties

The optical absorption spectra for undoped and Mn doped ZnS pellets which fabricated at room temperature by using hydraulic pressure, wavelength range 200-600 nm are shown in Fig.4. The optical spectra reveal that the absorption decreases with increase of wavelength as well as doping percent of Mn in ZnS pellets. Fig.4 shows that the ZnS is good absorption for wavelength range 200-300 nm. As doping percentage of Mn increases in pellets, the absorption edge shifted toward the higher wavelength side in pellets. A small shifted band indicates that the band gap decreases for doped ZnS pellets. Using these spectra, we determine the band gap of doped and undoped pellets. The band gap is obtained 3.3 eV and 3.5 eV respectively for Mn doped and undoped ZnS pellets. The band gap obtained in present investigation is similar with other investigators [21].

This sample may be used for fabrication in optical device which have needed low band at room temperature. These optical and structural properties arise due to quantum confinement effect resulting from the nanometer size of the particle.

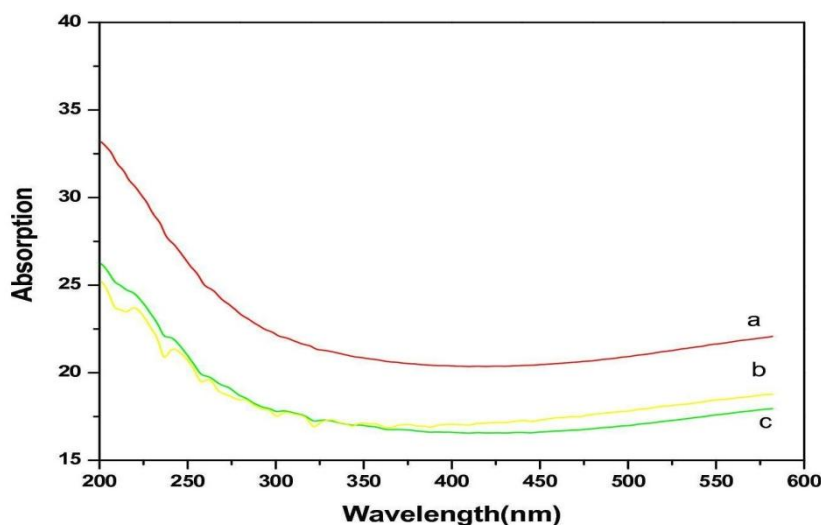


Fig. 4: UV-Vis Spectra (A) Undoped ZnS Pellet (B) 2% Mn Doped ZnS Pellet (C) 3 % Mn Doped ZnS Pellet

5. Conclusion

The ZnS pellets of manganese doped have been fabricated by hydraulic pressure. The grain size of the crystals for doped and undoped pellets have been evaluated and obtained maximum grain size 25.18 nm. SEM shows the agglomeration of nano-crystals. XRD analysis shows the sample prepared is in a cubical phase. The measurement of optical absorption spectra indicates that band gap shift with different percentage of Mn. The minimum band gap 3.3 eV has been observed.

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References

- [1] L.I. Li-ping, Q.I.U. Xiao-qing & L.I. Guang-she, Correlation between size-induced lattice variations and yellow emission shift in ZnO nanostructures, *J. Applied Physics Letters*, 87, (2005) pp. 4101-4109.
- [2] H. M. Schmidt, H. Weller, Synthesis of ZnS nanoparticles by solid liquid chemicals method, *J. Chemical Physics Letter*, 129, (1986) pp. 615-618. [http://dx.doi.org/10.1016/0009-2614\(86\)80410-9](http://dx.doi.org/10.1016/0009-2614(86)80410-9).
- [3] Y. Nasuno, N. Kohama, K. Nishimura, T. Hayakawa, H. Taniguchi and M. Shimizu, Size-dependent melting behavior of Zn nanowire arrays, *Applied Physics Letters*, 88(7), (2006) pp. 1909-1917.
- [4] L I Berger, Defect Evolution in Silicon Detector Material", Conference on Radiation Effects in Semiconductor Materials, Semiconductor Materials, (1996) pp. 186-190.
- [5] J.M. Hwang, Preparation and characterization of ZnS based nano-crystalline particles for polymer light-emitting diodes, *Current, Applied Physics*, 5 (1), (2005) pp. 31-34. <http://dx.doi.org/10.1016/j.cap.2003.11.075>.
- [6] H. Cho, Highly flexible organic light-emitting diodes based on ZnS/Ag/WO₃ multilayer transparent electrodes, *Organic Electronics*, 10 (6) (2009) pp. 1163-1169. <http://dx.doi.org/10.1016/j.orgel.2009.06.004>.
- [7] X.Liu, ZnS/Ag/ZnS nano-multilayer films for transparent electrodes in flat display application, *Applied Surface Science*, 183 (1-2), (2001) pp. 103-110. [http://dx.doi.org/10.1016/S0169-4332\(01\)00570-0](http://dx.doi.org/10.1016/S0169-4332(01)00570-0).
- [8] V. Dimitrova, J. Tate, Synthesis and characterization of some ZnS-based thin film phosphors for electroluminescent device applications, *Thin Solid Films*, 365 (1), (2000) pp.134-138. [http://dx.doi.org/10.1016/S0040-6090\(99\)01089-5](http://dx.doi.org/10.1016/S0040-6090(99)01089-5).
- [9] D.W. Wang, The improvement of near-ultraviolet electroluminescence of ZnO nanorods/MEH-PPV heterostructure by using a ZnS buffer layer, *Organic Electronics* 12 (1), (2011) pp. 92-97. <http://dx.doi.org/10.1016/j.orgel.2010.09.018>.
- [10] Z. G. Zhao, F. X. Geng, H. T. Cong, J. B. Bai & H. M. Cheng, A simple solution route to controlled synthesis of ZnS submicrospheres, nanosheets and nanorods *J.Nanotechnology*, 17, (2006) pp. 4731-4739. <http://dx.doi.org/10.1088/0957-4484/17/18/034>.
- [11] L. S Li and A. P Alivisatos, Semiconductor Nano rod Liquid Crystals and Their Assembly on a Substrate, *Adv. Mat.* 15, (2003) pp. 408-413. <http://dx.doi.org/10.1002/adma.200390093>.
- [12] Q Xiong, G. Chen, J. D Acord, X. Liu, J. J Zengel, H. R Gutierrez, J. M Redwing, L. C Lew Yan Voon, B. Lassen and P. C Eklund, Optical Properties of Rectangular Cross-sectional ZnS Nanowires, *Nano Lett.*, 4, (2004) pp. 1663-1668. <http://dx.doi.org/10.1021/nl049169r>.
- [13] Y. C. Zhu, Y. Bando and Y. Uemura, ZnS-Zn nanocables and ZnS nanotubes, *Chem. Commun.*, (2003) pp. 836-841. <http://dx.doi.org/10.1039/b300249g>.
- [14] Z. W. Pan, Z. R. Dai and Z.L Wang, Nanobelts of Semiconducting Oxides, *Science*, 291, (2001) pp. 1947-1952. <http://dx.doi.org/10.1126/science.1058120>.
- [15] S. Ghoshal, L. B Kumbhare, V. K Jain and G. K Dey, A facile synthesis of InSe (M = Cu, Ag) via low temperature pyrolysis of single source molecular precursors, [(R₃P)₂Min (SeCOAr)₄] *Bull.Mater. Sci.* 30, (2007) pp. 173-177. <http://dx.doi.org/10.1007/s12034-007-0031-8>.
- [16] A. B. Panda, G. Glaspell and M. S. El-Shall, Microwave Synthesis of Highly Aligned Ultra Narrow Semiconductor Rods and Wires, *J. Am. Chem. Soc.*, 128 (2006) pp. 2790-2797. <http://dx.doi.org/10.1021/ja058148b>.
- [17] Y. C. Zhang, G. Y. Wang, X. Y. Hu, Q. F. Shi, and Y. Yang, Phase-controlled synthesis of ZnS nanocrystallites by mild solvothermal decomposition of an air-stable single-source molecular precursor, *J. Cryst. Growth*, 284, (2005) pp. 554-560. <http://dx.doi.org/10.1016/j.jcrysgro.2005.07.023>.
- [18] C. Lu, Z. Cui, Z. Li, B Yang and J Shen, High refractive index thin films of ZnS/polythiourethane, *J. Mater. Chem.*, 13, (2003) pp. 526-531. <http://dx.doi.org/10.1039/b208850a>.
- [19] G. Kedarnath, V. K. Jain, S. Ghoshal, G. K Dey, C. An Ellis and R. T Tiepink, Zinc, Cadmium and Mercury Dithiocarboxylates: Synthesis, Characterization, Structure and Their Transformation to Metal Sulfide Nanoparticles, *Eur. J. Inorg. Chem.* (2007) pp. 1566-1572. <http://dx.doi.org/10.1002/ejic.200601059>.
- [20] H. Liu, Y. Ni, M. Han, Q. Liu, Z. Xu, and X. Ma, A facile template-free route for synthesis of hollow hexagonal ZnS nano- and submicrospheres, *Nanotechnology*, 16, (2005) pp. 2908-2912. <http://dx.doi.org/10.1088/0957-4484/16/12/030>.
- [21] R. Chauhan, A. Kumar and R. P Chaudhary, Characterization of chemically synthesized Mn doped ZnS nanoparticles, *Chalcogenide Letter*, 9, (2012) pp. 151-156.
- [22] C. S Pathak & M. K Mandal, Enhanced photoluminescence properties of Mn²⁺ doped ZnS nanocrystals, *Chalcogenide Letter*, 8, (2011) pp. 147-153.
- [23] R. N Bhargava, D. Gallagher, X. Hong & A. N. Urmikko, Optical properties of manganese doped nanocrystal of ZnS, *Phy.Rev.Lett.*, 72, (1994) pp. 416-421. <http://dx.doi.org/10.1103/PhysRevLett.72.416>.