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# CHEMICAL SHIELDING OF DOPED NITROGEN ON $C_{20}$ CAGE AND BOWL FULLERENES

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The $C_{20}$ (cage), $C_{20}$ (bowl), $C_{20}H_{10}$ (bowl) fullerene structures and their nitrogen doped derivatives such as $C_{20}NH$ (cage), $C_{20}NH$ (bowl), $C_{20}H_{10}N$ (bowl), $C_{20}H_{10}NH$ (bowl) are fully optimized at the MPW1PW91/6-31G level of theory. The natural atomic charge comparison shows that in $C_{20}H_{10}N$ (bowl), the nitrogen atom with about –0.58 has a more negative charge with respect to other nitrogen doped structures. The nuclear magnetic resonance chemical shielding is evaluated for nitrogen doped structures and the neighbors connected to nitrogen, $C_6$, and $C_7$ atoms. The nitrogen atom doped on carbon sites of $C_{20}H_{10}N$ (bowl) has the largest shielding isotropic shifts to the upper field (–203.58 ppm). This means that the electron density around nitrogen in the $C_{20}H_{10}N$ (bowl) structure is higher. Interestingly, there is a significant correlation between the charges and $\sigma_{\text{iso}}$ values of nitrogen and carbon atoms ($C_6$ and $C_7$). Namely, as the charge becomes more negative, $\sigma_{\text{iso}}$ shifts to the upper field. It is predicted that nitrogen doped $C_{20}H_{10}N$ (bowl) with the maximum electron density adopts this structure for electrophilic reactions.

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**Keywords:** $C_{20}$ (cage), $C_{20}$ (bowl), nitrogen doping, NMR.

Among different carbon clusters, $C_{20}$ is known as the smallest possible fullerene. There are pentagons with the highest symmetry $C_{20}$, which results in the extreme curvature and a high reactivity. Experimental studies of $C_{20}$ structures have established the existence of several arrangements. The experimental evidence of Prinzbach studies provided the existence of three different isomers of $C_{20}$: cage, bowl, and ring [ 1, 2 ]. There are no clear proofs as to which of the isomers is the most stable one. In 2013, Kharlamov and his coworkers reported the experimental synthesis of small carbon molecules ($C_3$—$C_{20}$) [ 3 ]. Sokolova′s studies on $C_{20}$ by different quantum mechanical methods showed the different total energies of $C_{20}$ isomers [ 4 ]. The bowl isomer of $C_{20}$ has the $C_{5v}$ symmetry with one central pentagon surrounded by five hexagons. The cage is formed exclusively by pentagons, but its symmetry has not yet been determined with certainty [ 5 ]. The $C_2$, $D_{2h}$, or $D_{3d}$ symmetry for the optimized geometry of the $C_{20}$ cage was found by different theoretical methods [ 6 ]. Based on DFT/LDA calculations, the cage isomer of $C_{20}$ has a geometry with the lowest energy, while DFT with gradient corrected exchange correlation functions as well as Hartree—Fock calculations predict the ring geometry to be the most stable one [ 4, 7 ]. According to the MP2/TZV2df calculation, the cage and bowl isomers of $C_{20}$ are almost isoenergetic and more stable than the ring isomer [ 8 ]. For the study of the geometrical structures of small fullerenes, NMR is a useful probe. The NMR parameters are related to the electronic structures of single molecules and can identify chemical changes. Many papers have reported the difference of fullerene isomers [ 9, 10 ] and fullerene-based materials [ 11 ] from NMR calculations. The theoretical calculations of NMR successfully fit the experimental results within a few ppm. Fowler has shown that the NMR technique is as accurate for fullerenes as for many other molecules and atomic clusters [ 12, 13 ]. Thus, the molecular structure can be estimated from the NMR peak positions and intensities. The NMR chemical shielding ($\sigma_{iso}$) is extremely sensitive to the local chemical environment of an atom [ 14, 15 ]. In this paper, we investigate the natural atomic charge distributions by the natural bond orbital (NBO) method and the NMR parameters of $C_{20}$ fullerene isomers (cage and bowl) and their doped nitrogen derivatives using MPW1PW91/6-31G.

**Computational details.** In the present study, we doped a nitrogen atom to $C_{20}$ (cage) fullerene and $C_{20}$ (bowl) fullerene with and without a hydrogen atom terminated at different positions to find the more stable structure; and then the effects of nitrogen doping on the structural properties were investigated. We calculated the isotropic magnetic shielding of the structures. The NMR properties were performed within the gauge-independent atomic orbital (GIAO) approach [ 16 ]. The full geometry optimizations and NMR calculations of pristine and N-doped fullerene $C_{20}$ cage and bowl molecules were performed using DFT [ 17 ] at the MPW1PW91 level (Barone′s Modified Perdew—Wang 1991 exchange functional and Perdew and Wang′s 1991 correlation functional) [ 18 ] with the 6-31G basis set. MPW1PW91 is a new hybrid Hartree—Fock density functional (HF-DF) model that produces remarkable results for both covalent and non-covalent interactions [ 19 ]. The calculations are performed by the GAUSSIAN 98 program package [ 20 ].

**Results and discussion.** The structures of $C_{20}$ (cage) (Fig. 1, *a*), $C_{20}$ (bowl) (Fig. 1, *b*), $C_{20}H_{10}$ (bowl) (Fig. 1, *c*), and their nitrogen doped derivatives $C_{20}NH$ (cage) (Fig. 1, *d*), $C_{20}NH$ (bowl) (Fig. 1, *e*), $C_{20}H_{10}N$ (bowl) (Fig. 1, *f*), and $C_{20}H_{10}NH$ (bowl) (Fig. 1, *g*) were optimized at the MPW1PW91 level with the 6-31G(*d*) basis set. The total energies and natural atomic charge distributions (obtained by the NBO analysis) of the optimized structures in the nitrogen doped derivatives and the neighboring $C_6$ and $C_7$ atoms bonded to the nitrogen atom are listed in Table 1. The energies of three possible configurations of nitrogen doped bowl structures such as $C_{20}H_{10}N$ (bowl), $C_{20}H_{10}NH$ (bowl) and $C_{20}NH$ (bowl) are found. It is clear that, the comparison of energies of all structures is not logical because of a difference in the number of atoms. However, the structures of $C_{20}$ (cage) and $C_{20}$ (bowl) and also $C_{20}NH$ (cage) and $C_{20}NH$ (bowl) can be compared.

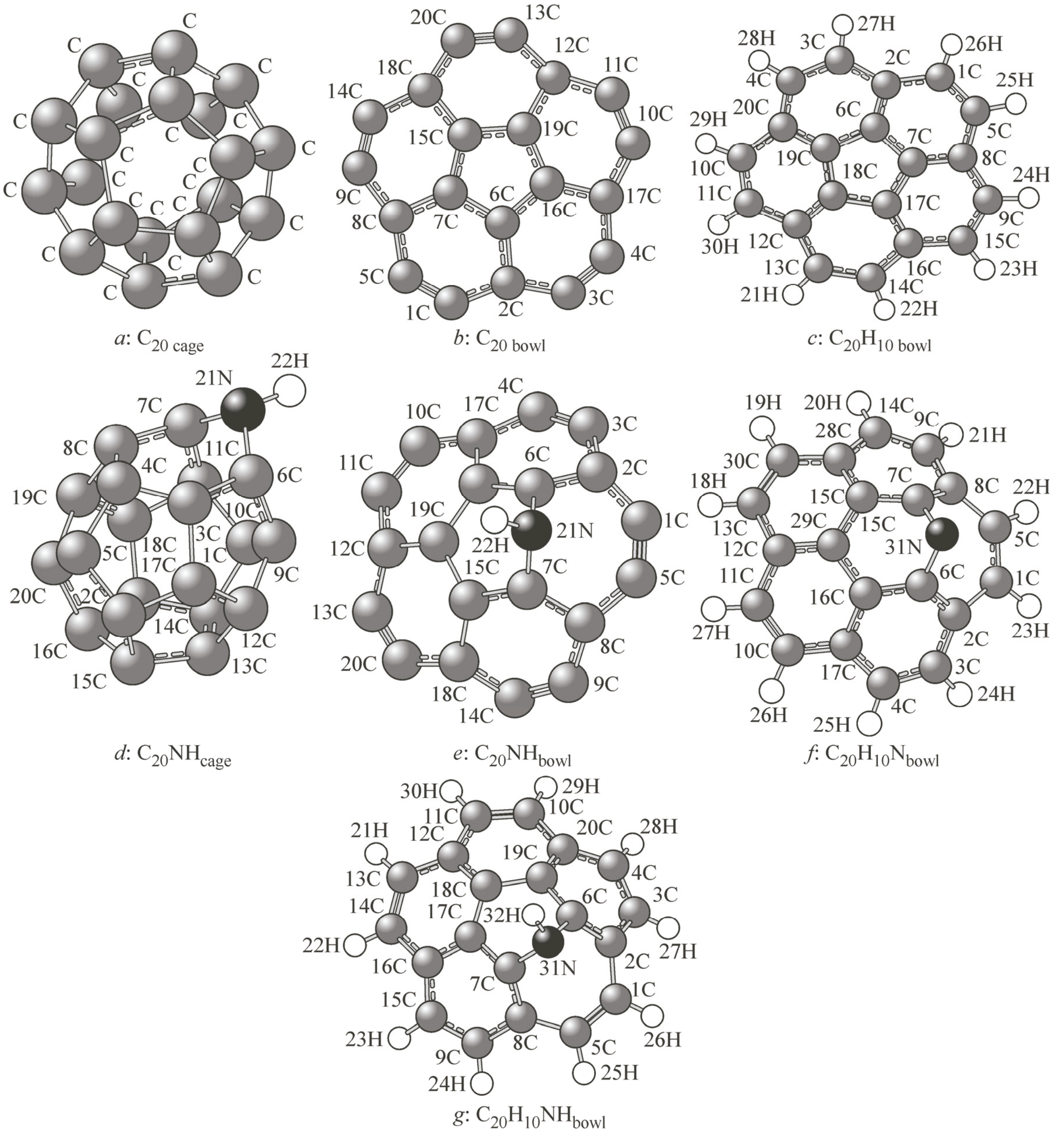
The *m*PW1PW91/6-31G(*d,p*) optimized total energies (Table 1) suggest that $C_{20}$ (bowl) is more stable than $C_{20}$ (cage) by 23.87 kcal/mol, and $C_{20}NH$ (cage) is more stable than $C_{20}NH$ (bowl) by 37.65 kcal/mol (1 a.u. is 627.25 kcal/mol).

The natural atomic charges presented in Table 1 show that the charges on $C_6$ and $C_7$ carbon atoms significantly deviate from the initial values for the corresponding carbon atoms in undoped fullerene. For example, the charges on $C_6$ and $C_7$ sites range from –0.001 in $C_{20}$ (cage) to +0.102 in $C_{20}NH$ (cage), whereas those carbon atoms have negative charges in the all bowl fullerenes. In $C_{20}H_{10}$ (bowl), the charges of $C_6$ and $C_7$ are about –0.074 and a distinct change is not observed for $C_{20}H_{10}NH$ (bowl), while those of $C_{20}H_{10}N$ (bowl) are most negative, about –0.134. The nitrogen doping effect on the charges of $C_6$ and $C_7$ ranging from –0.07 in $C_{20}$ (bowl) to –0.03 in $C_{20}NH$ (bowl), is not significant either. Also, the comparison of charges on the nitrogen atom shows that in $C_{20}H_{10}N$ (bowl) the nitrogen atom with about –0.58 has a more negative charge with respect to other nitrogen doped structures.

Table 1

*Total energies of the structures* ($E_{tot}$, a.u.) *and natural atomic charges of* N, $C_6$, *and* $C_7$ *at the m*PW1PW91/6-311G(*d,p*) *level*

| Structure | $C_{20\ cage}$ | $C_{20}H_{10\ bowl}$ | $C_{20\ bowl}$ | $C_{20}NH_{cage}$ | $C_{20}H_{10}N_{bowl}$ | $C_{20}H_{10}NH_{bowl}$ | $C_{20}NH_{bowl}$ |
|---|---|---|---|---|---|---|---|
| $E_{tot}$ | –761.069 | –767.810 | –761.107 | –816.430 | –822.407 | –823.0627 | –816.376 |
| $Q_N$ | — | — | — | –0.57374 | –0.58437 | –0.51834 | –0.50127 |
| $Q_{C6}$ | –0.00122 | –0.07442 | –0.07442 | 0.10285 | –0.13413 | –0.07251 | –0.03583 |
| $Q_{C7}$ | –0.00093 | –0.07429 | –0.14380 | 0.102846 | –0.13334 | –0.07251 | –0.03616 |



*a*: $C_{20\ \mathrm{cage}}$ *b*: $C_{20\ \mathrm{bowl}}$ *c*: $C_{20}H_{10\ \mathrm{bowl}}$

*d*: $C_{20}NH_{\mathrm{cage}}$ *e*: $C_{20}NH_{\mathrm{bowl}}$ *f*: $C_{20}H_{10}N_{\mathrm{bowl}}$

*g*: $C_{20}H_{10}NH_{\mathrm{bowl}}$

*Fig. 1.* Fullerene structures: $C_{20\ \mathrm{cage}}$ (*a*), $C_{20\ \mathrm{bowl}}$ (*b*), $C_{20}H_{10\ \mathrm{bowl}}$ (*c*), $C_{20}NH_{\mathrm{cage}}$ (*d*), $C_{20}NH_{\mathrm{bowl}}$ (*e*), $C_{20}H_{10}N_{\mathrm{bowl}}$ (*f*), and $C_{20}H_{10}NH_{\mathrm{bowl}}$ (*g*)

Therefore, one can now conclude that the charge distribution around the nitrogen atom in $C_{20}H_{10}N$ (bowl) is greater than the others. The calculated chemical shielding tensors are converted to measurable NMR parameters, isotropic chemical shielding ($\sigma_{\mathrm{iso}}$), using the following equation [21, 22]:

$$\sigma_{\mathrm{iso}}(\mathrm{ppm}) = \frac{(\sigma_{11} + \sigma_{22} + \sigma_{33})}{3}, \tag{1}$$

where $\sigma_i$'s are the eigenvalues of the symmetrized NMR shielding matrix, ordered according to $\sigma_{11} < \sigma_{22} < \sigma_{33}$. The following section describes our results in terms of the NMR chemical shielding that has a contribution of the chemical environment of the atom [23]. In NMR spectroscopy, the standard system is chosen as the reference, thus, the chemical shielding is taken as the shielding difference between the atom of interest and the corresponding atom in the reference system [24]. In the theoretical calculations, the magnetic shielding must then be subtracted from the shielding in the

Table 2

*Isotropic chemical shielding* ($\sigma_{iso}$, ppm) *of* $C_6$, $C_7$, *and nitrogen atoms for pristine and nitrogen doped* $C_{20\ cage}$ *and* $C_{20\ bowl}$ *at the m*PW1PW91/6-311G(*d*,*p*) *level*

| Structure | $C_{20\ cage}$ | $C_{20}H_{1\ bowl}$ | $C_{20\ bowl}$ | $C_{20}NH_{cage}$ | $C_{20}H_{10}N_{bowl}$ | $C_{20}H_{10}NH_{bowl}$ | $C_{20}NH_{bowl}$ |
|---|---|---|---|---|---|---|---|
| $\sigma_{iso\ N}$ | — | — | — | 153.04 | –203.584 | 195.122 | 165.94 |
| $\sigma_{iso\ C6}$ | 44.83 | 66.89 | 50.50 | –35.31 | 42.473 | 67.365 | 59.548 |
| $\sigma_{iso\ C7}$ | 45.15 | 66.89 | 50.50 | –35.39 | 42.473 | 67.365 | 59.548 |

reference system. Thus, the chemical shielding is simply referred as the comparison between the shielding of the carbon atom in $C_{20}N$ (cage or bowl) and the shielding of the carbon atom in $C_{20}$ (cage or bowl).

Nitrogen is more electronegative than carbon, therefore the $C_6$ and $C_7$ sites directly bonded to to N show completely different behaviors, therefore we focus on the doped nitrogen atom and the neighbors bonded to nitrogen, $C_6$, and $C_7$ atoms indicated in Fig. 1.

Our calculated chemical shielding for the carbon atoms ($C_6$, $C_7$) in $C_{20}$ (cage) corresponding to the nitrogen doped positions are 44.83 ppm and 45.15 ppm, respectively. The $C_6$ and $C_7$ atoms on the pentagonal ring in $C_{20}H_{10}$ (bowl) and $C_{20}$ (bowl) are equivalent. The chemical shielding of $C_6$ and $C_7$ are 66.89 ppm and 50.50 ppm in $C_{20}H_{10}$ (bowl) and $C_{20}$ (bowl), respectively. These reference values are used to evaluate the chemical shielding of $C_6$ and $C_7$ in the other structures.

As can be seen in Table 2, $C_6$ and $C_7$ (bonded to nitrogen) of $C_{20}NH$ (cage) (Fig. 1, *d*) give $\sigma_{iso}$ of –35.3 ppm, thus showing that more shielded atoms in $C_{20}NH$ (cage) are shifted upfield with respect to these atoms in $C_{20}$ (cage).

The comparison of $\sigma_{iso}$ parameters of two $C_{20}H_{10}$ (bowl) and $C_{20}H_{10}NH$ (bowl) structures (Fig. 1, *b*, *f*), which are given in Table 2, show that the chemical shielding of $C_6$ and $C_7$ is approximately equivalent, (about 67 ppm) in the downfield region. Our results show that the values of $\sigma_{iso}$ parameter for $C_6$ and $C_7$ of all bowl $C_{20}$ structures ($C_{20}H_{10}$ (bowl), $C_{20}$ (bowl), $C_{20}H_{10}N$ (bowl), $C_{20}H_{10}NH$ (bowl), $C_{20}NH$ (bowl)) are positive, which indicates the smaller shielding on $C_6$ and $C_7$.

The $\sigma_{iso}$ values of a nitrogen atom doped to the carbon sites ($C_6$ and $C_7$) of $C_{20}H_{10}N$ (bowl) with the largest isotropic shielding are shifted upfield (–203.58 ppm). This means that the electron density around the nitrogen atom in this structure is higher, which indicates that a shielding effect on this atom is high, whereas the chemical shielding of the nitrogen atom shifts downfield for the other structures as a result of the decreased shielding in this region. Interestingly, there is a significant correlation between the charges and $\sigma_{iso}$ values of nitrogen and carbon ($C_6$ and $C_7$) atoms, namely, as the charge becomes more negative, $\sigma_{iso}$ shift to the upper field. We can see that when the atom has a more negative charge, it is more shielded, so that the $C_6$, $C_7$, and nitrogen atoms in $C_{20}H_{10}N$ (bowl), which have the most negative charges (Table 1), are the most shielded atoms in comparison with the corresponding reference (Table 2).

**Conclusions.** The seven different structures of $C_{20}$ (cage), $C_{20}$ (bowl) and their nitrogen doped derivatives were optimized at the MPW1PW91 level with the 6-31G(*d*) basis set. The comparison of natural atomic charges on the nitrogen atom shows that in $C_{20}H_{10}N$ (bowl), the nitrogen atom with about –0.58, has a more negative charge with respect to other nitrogen doped structures. Our results show that the values of the $\sigma_{iso}$ parameter for $C_6$ and $C_7$ of all bowl $C_{20}$ structures ($C_{20}H_{10}$ (bowl), $C_{20}$ (bowl), $C_{20}H_{10}N$ (bowl), $C_{20}H_{10}NH$ (bowl), $C_{20}NH$ (bowl)) are positive, which indicates the smaller shielding on $C_6$ and $C_7$.

The nitrogen atom doped to carbon sites ($C_6$ and $C_7$) of $C_{20}H_{10}N$ (bowl) with the largest isotropic shielding shifts upfield (–203.58 ppm). This means that the electron density around the nitrogen atom in this structure is higher, which indicates that the shielding effect on this atom is high, whereas the chemical shielding on the nitrogen atom shifts downfield for other structures as a result of the decreased shielding in this region. There is a significant correlation between the charges and $\sigma_{iso}$ values of nitrogen and carbon atoms. It is predicted that the nitrogen atom doped to $C_{20}H_{10}N$ (bowl) with the maximum electron density adopts this structure for electrophilic reactions.

## *REFERENCES*

1. *Prinzbach H., Weiler A., Landenberer P.* // Nature. – 2000. – **407**. – P. 60 – 63.
2. *Wahl F., Wörth J., Prinzbach H.* // Angew. Chem., Int. E. – 1993. – **32**. – P. 1722 – 1726.
3. *Prinzbach H., Weber K.* // Angew. Chem., Int. Ed. – 1994. – **33**. – P. 2239 – 2257.
4. *Kharlamov A.* // Chem. Engineer. Sci. – 2013. – **3**. – P. 32 – 40.
5. *Sokolova S., L€uchow A., Anderson J.B.* // Chem. Phys. Lett. – 2000. – **323**. – P. 229 – 233.
6. *Saito M., Miyamoto Y.* // Phys. Rev. Lett. – 2001. – **87**. – P. 035503-1.
7. *Romero A.H., Sebastiani D.* // Chem. Phys. Lett. – 2002. – **366**. – P. 134 – 140.
8. *Grossmann J.C., Mitas L., Raghavachari K.* // Phys. Rev. Lett. – 1995. – **75**. – P. 3870 – 3873.
9. *Grimme S., Muck-Lichtenfeld C.* // Chem. Phys. Chem. – 2002. – **2**. – P. 207 – 209.
10. *Galli G., Gygi F., Golaz J.C.* // Phys. Rev. B. – 1998. – **57**. – P. 1860 – 1867.
11. *Jones R.O., Seifert G .* // Phys. Rev. Lett. – 1997. – **79**. – P. 443 – 446.
12. *Birkett P.R., Bühl M., Khong A., Saunders M., Taylor R.* // J. Chem. Soc. Perkin Trans. – 1999. – **2**. – P. 2037 – 2039.
13. *Fowler P.W., Lazzeretti P., Malagoli M., Zanasi R.* // Chem.Phys. Lett. – 1991. – **179**. – P. 174 – 180.
14. *Fath-Tabar G.H., Ashrafi A.R., Stevanovic D.* // J. Comput. Theor. Nanosci. – 2012. – **9**. – P. 327 – 329.
15. [a] *Hrobárik P., Reviakine R., Arbuznikov A.V., Malkina O.L., Malkin V.G.* // J. Chem. Phys. – 2007. – **126**. – P. 024107. [b] *Pennanen T.O., Vaara J.* // Phys. Rev. Lett. – 2008. – **100**. – P. 2411 – 2412.
16. *Harigaya K.* // J. Comput. Theor. Nanosci. – 2012. – **9**. – P. 347 – 350.
17. *Wolinski K., Hilton J.F., Pulay P.* // J. Am. Chem. Soc. – 1990. – **112**. – P. 8251 – 8260.
18. *Parr R.G., Yang W.* Density-Functional Theory of Atoms and Molecules. – Oxford: Oxford University Press, 1989.
19. *Adamo C., Barone V.* // J. Chem. Phys. – 1998. – **108**. – P. 664 – 675.
20. *Lynch B.J., Fast P.L., Harris M., Truhlar D.G.* // J. Phys. Chem. A. – 2000. – **104**. – P. 4811 – 4815.
21. *Frisch M.J., Trucks G.W., Schlegel H.B., Scuserial G.* // Gaussian 98, Revision A.7, Gaussian, 1998. – Inc., Pittsburgh PA.
22. *Drago R.S.* Physical Methods for Chemists. – Florida: Saunders College Publishing, 1992.
23. *Hafied M., Belloum M.* // J. Comput. Theor. Nanosci. – 2012. – **9**. – P. 77 – 82.
24. *Sebastiani D., Parrinello M.* // J. Phys. Chem. A. – 2001. – **105**. – P. 1951 – 1058.
25. *Rezaei-Sameti M.* // Quantum Matter. – 2013. – **2**. – P. 396 – 400.