FACTORS INFLUENCING THE MICROSTRUCTURE AND MAGNETISM OF IRON NANOPARTICLES

NGUYEN TRONG DUNG[*] , NGUYỄN CHÍNH CƯƠNG[**]

ABSTRACT

This paper studies factors that influencing the microstructure of the iron nanoparticles using Molecular Dynamics (MD) method with the Pak – Doyama pair interaction potential and aperiodic boundary conditions. Factors that influencing the magnetism using the Ising model with Metropolis algorithm. The results were analyzed through the radial distribution functions (RDF), the average coordination number, the size of particles, the energy and the relationship between magnetic moment and curie temperature. The results show that there were influences of factors such as the temperature, the phase state, the crystallization and the core radius of the iron nanoparticles on the microstructure and the magnetism of the model.

Keywords: Microstructure, magnetism, iron nanoparticles, Molecular Dynamics (MD) simulation.

TÓM TẮT

Các yếu tố ảnh hưởng lên vi cấu trúc, từ tính của hạt nano sắt

Bài báo này nghiên cứu các yếu tố ảnh hưởng lên vi cấu trúc của hạt nano sắt bằng phương pháp động lực học phân tử (MD) với thế tương tác cặp Pak-Doyama, điều kiện biên không tuần hoàn. Các yếu tố ảnh hưởng lên từ tính bằng mô hình Ising với thuật toán Metropolis. Các kết quả nghiên cứu được phân tích thông qua hàm phân bố xuyên tâm (RDF), số phối trí trung bình, kích thước hạt, năng lượng và mối quan hệ giữa momen từ và nhiệt độ curie. Nghiên cứu này cho thấy có sự ảnh hưởng của các yếu tố như nhiệt độ, trạng thái pha, tỉ lệ tinh thể hóa, bán kính lõi hạt nano sắt lên vi cấu trúc và từ tính của mô hình.

Từ khóa: Vi cấu trúc, từ tính, hạt nano sắt, mô phỏng động lực học phân tử.

1. Introduciton

Iron nanoparticles have wide applications in sciences, technologies and life such as: photonics, electronics, catalysis, biomedicines etc [2]. Thus the iron nanoparticles are considered as one of the important subjects of scientific research activities. There have been different methods to study the microstructure and the magnetism of the iron nanoparticles.. Some theoretical methods can be used the Dynamical Mean Field Theory (DMFT) [8]. Experimental methods may use X-rays (XPS) to determine the composition of the nano particles [6], the size of the nano particles and the

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microstructure of the nano particles [11]. Besides, in recent years, the Molecular Dynamics (MD) simulation method has been used to determine the crystallization process [7] and the Monte Carlo simulation method to determine the compensation temperature [10].

The causes of the appearance of the compensation temperature in the nano-iron models are the same. For the iron nanoparticles, the iron nano-wire and the iron nano-tube, the presence of the compensation temperature was due to the antiferro magnetic interaction between the magnetic moment of the core layer and the shell layer (even when there was the same magnetic moment in the core layer and the shell layer). The relationship between the magnetism and the particle size, the crystallization process and the exchange integral between the core layer and the shell layer was also determined by simulating the models. Today, with the aid of computers, the size of the studied models was significantly increased.

We used the nano-iron model to study the influence of these factors on the microstructure and the magnetism of the iron nanoparticles. The study methods and calculations are presented in part 2, the results and discussions are presented in part 3. Part 4 is the conclusion of the research contents.

2. Caculation method

The iron nanoparticles model was established on the basis of using the Dynamics equation F = ma of the atoms (molecules). When the atoms (molecules) moved, we could identify the factors that influence the microstructure and the magnetism such as: the temperature, the phase state, the crystallization ratio, the core radius of the nano particles. In the simulation, we chose the Pak - Doyama pair interaction potential (1) and aperiodic boundary conditions for nano-iron sample [9]

$$U(r) = -0.188917(1.82709 - r)^4 + 1.70192(r - 2.50849)^2 - 0.198294;\ r < 3.44\,\text{Å} \quad (1)$$

The nano-iron samples with 10,000 particles at temperatures of 300K, 500K, 700K and 900K were studied on the basis of examining the influence of the temperature, the phase state, the ratio of crystallization and the core radius of the nano particles on the microstructure using Molecular Dynamics method with the Pak - Doyama pair interaction potential and aperiodic boundary conditions. The microstructure characteristics were analyzed through the radial distribution functions, the average energy, the size of the nano particles and the average coordination number.

In addition, the magnetism of the nano particles was analyzed through the Ising model with Metropolis algorithm, then the structural phase transition temperature was determined by (2) [4]:

$$T_B = \left(\frac{KV}{25k_B}\right) = K\left(\frac{4\pi r_0^{\,3}}{3}\right)\frac{1}{25k_B} \quad (2)$$

When the size of the nano particles decreased, the iron nanoparticles tended to turn from the ferromagnetic state to the super paramagnetic state. Then the critical size of the nano particles had the following form (3) [3]:

$$r_0 = \left(\frac{6k_BT_B}{K}\right)^{\frac{1}{3}};\ T_C = \frac{1}{k_BT_B};\ \mathrm{k_B} = 8.617(15).10^{-5}\ \mathrm{J/mol.K} \quad (3)$$

With, r_0 is the critical size of nanoparticles from the ferromagnetic state into the superparamagnetic state, k_B is Boltzmann's constant, T_B is the phase transition temperature from the ferromagnetic state to the super paramagnetic state or temperature models, T_C is the curie temperature, K is a constant and V is the volume of a nano particle.

The change in the size of the nano particles which led to the change of the magnetization to a constant value was called the saturated magnetization. These quantities related to each other by the formula (4) [5].

$$\frac{r-d}{r} = \left(\frac{M_s}{M_{sb}}\right)^{\frac{1}{3}} \rightarrow\ r_{loi} = \left(\frac{M_s}{M_{sb}}\right)^{\frac{1}{3}} r \quad (4)$$

In which: r is the radius of the nano particles, d is the thickness of the shell layer, M_{sb} is the saturated magnetization of the bulk sample, M_s is the saturated magnetization of the nano particles. In experiment, the curie temperature of the iron α at room temperature is 1,044K [2].

The interaction of spins in the shell layer or in the core layer was called the ferromagnetic interaction while the interaction of spins between the shell layer and the core layer was called the antiferromagnetic interaction. Results showed that there was an influence of the temperature, the phase state, the crystallization ratio and the core radius of the nano particles on the microstructure and the magnetism. These results were considerably consistent with results from recent studies.

3. Results and disscusions

The microstructure of the iron nanoparticles was studied by Molecular Dynamics (MD) method with Pak - Doyama pair interaction potential and appropriate boundary conditions at temperatures of 300 K, 500 K, 700 K, 900 K and 1,000 K. Their shape and size are presented in Figure 1 and Table 1.

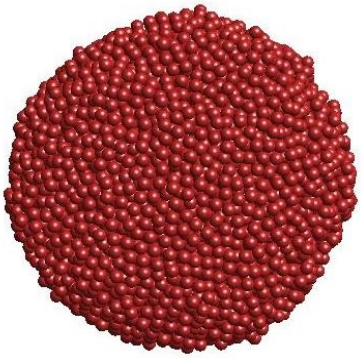

Figure 1. *The shape of the iron nanoparticles at temperature of 300K*

Table 1. *The size of the iron nanoparticles at different temperatures*

Temperature (K)	300	500	700	900	*1,000*
Particle size (nm)	*3.337*	*3.358*	*3.385*	*3.362*	*3.424*

The results in Figure 1 and Table 1 show that the nano-iron sample had the spherical shape and nano size. The size of the iron nanoparticles increased sharply when the temperature was increased, it increased from 3.337nm to 3.424nm when the temperature was increased from 300K to 1,000K. The microstructure of the iron nanoparticles was studied at different temperatures and results are shown in Figure 2.

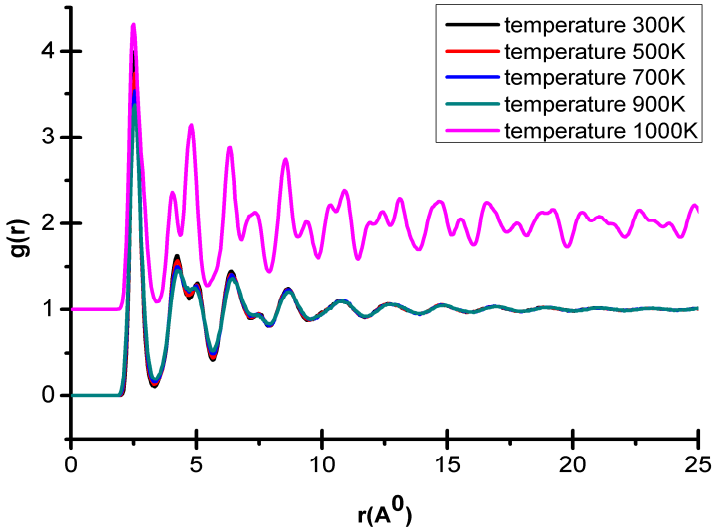

Figure 2. *Radial distribution functions of the iron nanoparticles at different temperatures*

The results in Figure 2 show that the first peak of the radial distribution functions prevailed in the iron nanoparticles at the temperatures of 300K, 500K, 700K, 900K and 1,000K. When the temperature was increased, the value of the first peak position of the radial distribution functions changed slightly, this proved that the internal distance between atoms (molecules) did not depend on the temperature and only a close order existed in the coupling of the iron nanoparticles. When the temperature was increased, the density of the atoms (molecules) decreased because the first peak height of the radial distribution functions tended to decrease when the temperature increased. Obviously, there was an influence of the temperature on the heterogeneous properties of the microstructure in the iron nanoparticles.

Observing the sample at the temperature of 1,000 K, we see that there was a peak separation in the second peak of the radial distribution functions which generated two small peaks. This showed us there was a phase transition from the amorphous state to the crystalline state in the model at this temperature range. To continue the study, we investigated the coordination number (Figure 3) and the energy (Table 2) of the model.

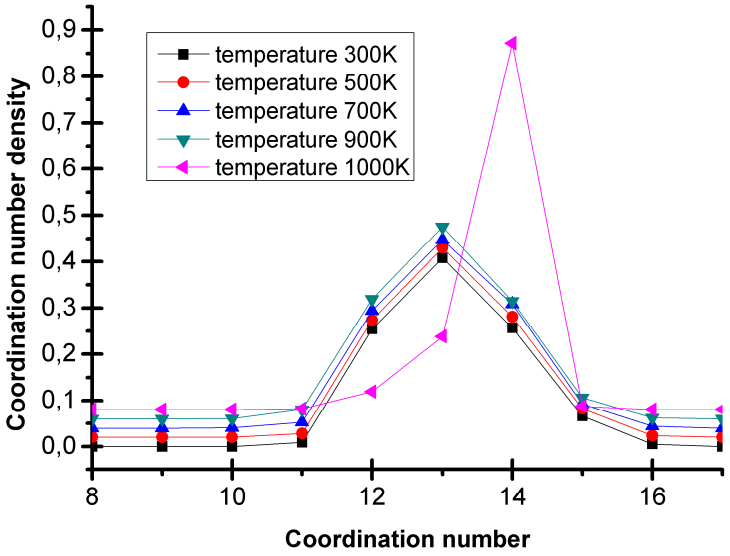

Figure 3. *The coordination number of the nano particles at different temperatures*

Table 2. *The energy of the iron nanoparticles at different temperatures.*

Temperature (K)	300	500	700	900	1,000
Energy (eV)	-1.289	-1.235	-1.179	-1.119	-1.120

Observing Figure 3 and Table 2, we see that the coordination numbers of the iron nanoparticles at temperature of 300 K and 900 K were both number 13. At temperatures of 1000 K, the coordination numbers moved to the location number 14. At 1000K temperature of the iron nanoparticles energy decreases and the density of coordination number increased. This showed us the crystallization occurred in the iron nanoparticles at the temperature from 900 K to 1,000K. The influence of temperature on the microstructure was caused by the heterogeneity in the iron nanoparticles.

To ascertain the crystallization in the iron nanoparticles at the temperature range 900 K and 1,000 K, we used the visualization method to observe the crystallization process at different temperatures. The results are shown in Figure 4.

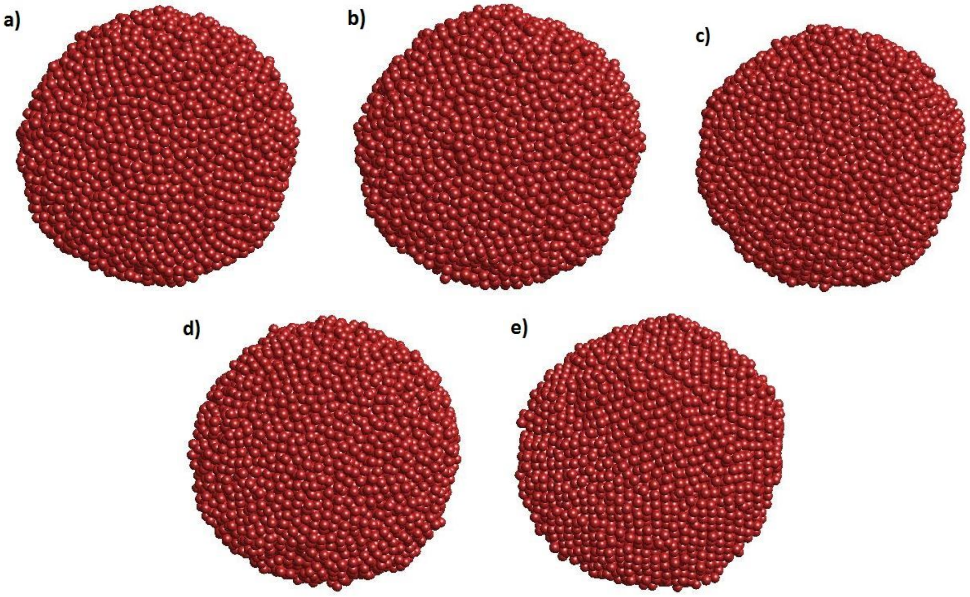

Figure 4. *The shapes of the iron nanoparticles at different temperatures*
a) 300 K; b) 500 K; c) 700 K; d) 900 K; e) 1,000 K

Observing Figure 4 we see that the iron nanoparticles had spherical shapes.

When the temperature was increased from 300 K to 1,000 K the size iron nanoparticles tended to dilate and the atoms (molecules) turned from the amorphous state to the crystalline structure state. Thus, we can ascertain the apparent influence of the temperature on the microstructure of the iron nanoparticles.

To examine the temperature range in which the crystallization process occurred, we focused on examining the iron nanoparticles sample at the temperature 900 K (because this sample has energy fluctuations and favorable conditions for the crystallization process), and results are shown in Figure 5.

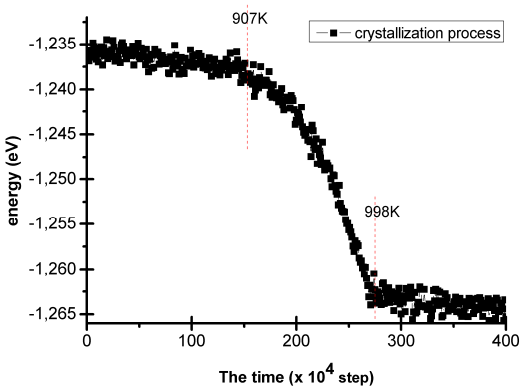

Figure 5. *The crystallization process of the sample at 900 K*

Figure 5 shows that with the number of step smaller than $1{,}5.10^6$ steps (corresponding to the temperature at 907 K), the crystallization energy changed insignificantly (it was almost equal between the crystal nucleation production and annihilation process). When the number of thermal annealing step was increased to $2{,}7.10^6$ steps (corresponding to the temperature at 998 K), the crystallization energy reduced dramatically, the result was almost linear which corresponded to the temperature from 907 K to 998 K. That confirms the crystallization temperature range was between 907 K and 998 K.

The above results showed that there was significant influence of the temperature and the number of thermal annealing step on the microstructure and the crystallization process in iron nanoparticles models. The mechanism of the crystallization process was as follows:

When the number of thermal annealing step was increased, the energy of samples reduced. This made the crystals focused on areas with low energy leading to the formation of crystals nucleation.

The crystal nucleation formation process continued to occur until there was only the interaction between crystal nucleations in the sample, then the crystallization occurred entirely in the sample.

To study the magnetism of nano particles, we investigated the influence of the core radius on the magnetism. The results are shown in Figure 6, Table 3

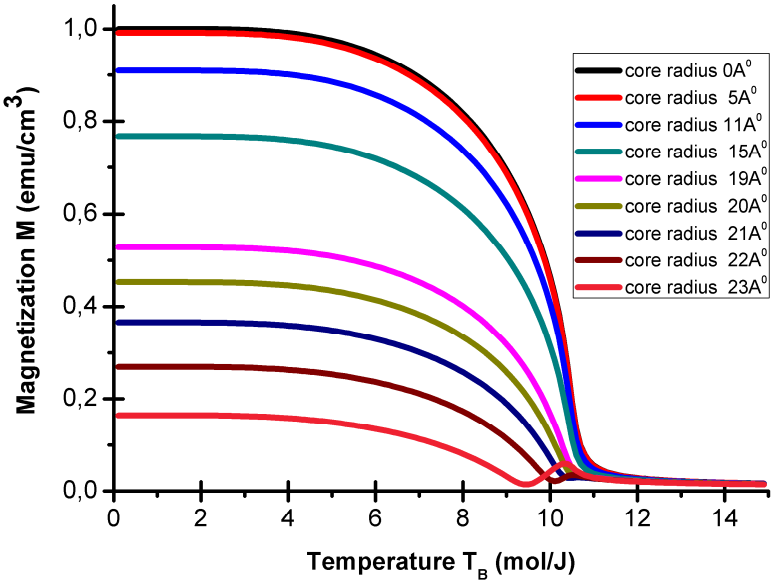

Figure 6. *The magnetism of the iron nanoparticles with different core radius*

Table 3. *The phase transition temperature of the iron nanoparticles with different core radius*

Core radius (A^0)	0	5	11	15	19	20	21	22	*23*
Magnetization M (emu/cm^3)	1	0.9914	0.9094	0.7672	0.5284	0.4528	0.3656	0.2692	0.1642
Temperature models T_B (mol/J)	10.5	10.5	10.5	10.45	10.35	10.25	10.1	10.5	10.5
Temperature curie Tc (K)	1,105.2	1,105.2	1,105.2	1,110.5	1,121.2	1,132.17	1,148.9	1,105.2	1,105.2

The results in Figure 6, Table 3 show that with the core radius which was smaller than 22 A^0 transition temperature of models decrease from 10.5 to 10.1 corresponding curie temperature increased from 1105.2K to 1148.9 K. When the core radius was increased which led to the decrease of the magnetization and the of the increase curie temperature. To determine the core radius of the nano particles, we chose a location at which start appearing temperature compensation corresponding to the location with the magnetization 0.2692, then:

$$r_{loi} = \left(\frac{M_s}{M_{sb}}\right)^{\frac{1}{3}} r \text{ ; Ms = 0.2692, Msb = 1, r = 33.45A} \rightarrow r_{loi} = 21.5\ A^0$$

The chosen location using the simulation method gave the biased result of 2.3%. The chosen core radius location of 22 A^0 was totally appropriate. We continued to study the influence of the temperature with the chosen core radius of 22 A^0. The results are shown in Figure 7.

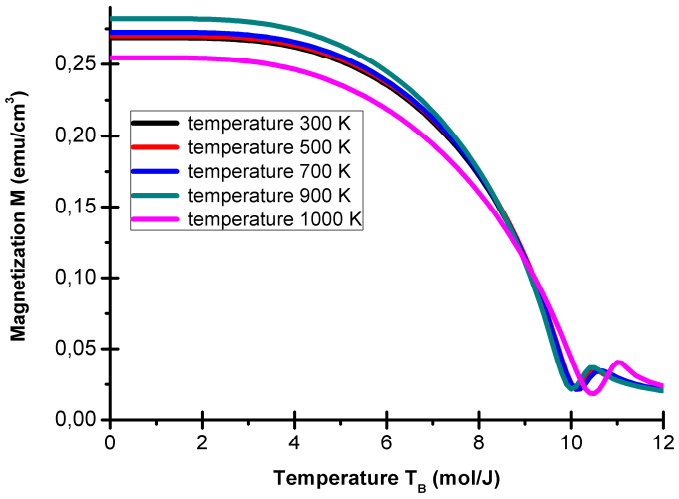

Figure 7. *The magnetism of the iron nanoparticles at different temperatures*

Result in Figure 7 shows that the magnetization of nano particles increased when increased temperature. The phase transition temperature was 10.1 K in the samples with the temperature of 300 K and 900 K corresponding to the curie temperature T_{C1} = 1,148.9K. For the temperature range 1,000 K, the phase transition temperature was 10.5 K corresponding to the curie temperature T_{c2} = 1,105.2 K.

This shows that the curie temperature of the iron nanoparticles increased in the temperature range 1,000 K. This result was entirely consistent with the results from analyzing the microstructure of the iron nanoparticles because the crystallization occurred at this temperature range.

Thus, the temperature of the sample did not affect the transition temperature which affects only the magnetization. To ascertain this, we continued to examine the influence of the crystallization process on the magnetism of the iron nanoparticles model. The results are shown in Figure 8.

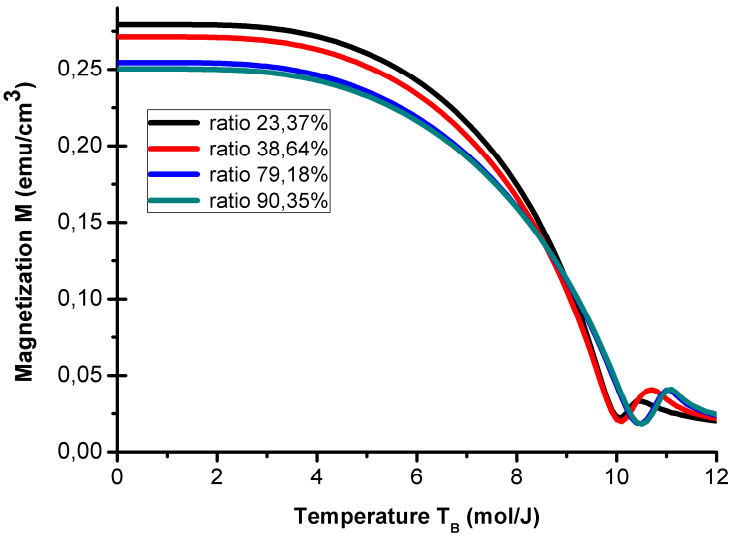

Figure 8. *The magnetism of iron nanoparticles with different ratio of crystallization*

Figure 8 shows us when the crystallization ratio increased, the magnetization of the iron nanoparticles samples decreased, the phase transition temperature increased which led to the decrease of the curie temperature.

That shows factor influence main to microstructure, magnetic of nanoparticles iron is due the size effect caused. As the temperature rises resulting radius, energy of the model increases reduces density of atoms (molecules) and appear crystalline state. As the radius, crystallization increases leads to magnetization decrease and temperature curie increases.

4. Conclusions

Results from studying the influence of the temperature, the phase state, the crystallization ratio and the core radius of the nano particles on the microstructure and the magnetism of the iron nanoparticles are as follows:

- We have successfully established the iron nanoparticles sample with 10^4 particles with spherical shape by Molecular Dynamics method with the Pak - Doyama pair interaction potential and aperiodic boundary conditions. Results are consistent with experimental results.

- The influence of the temperature, the phase state, the crystallization ratio and the core radius of the nano particles on the microstructure and the magnetism of the nano-iron sample have been determined.

- The phase states of the nano-iron sample have been identified as the amorphous state at temperatures of 300 K, 500 K, 700 K, 900 K and as the crystalline state at temperatures of 1,000 K.

- The crystallization process has been determined by the separation of the peak at the second peak of the radial distribution functions with coordination number 14.

- Determining temperature zones occur crystallization process from 907 K to 998 K.

- The factors that influence the magnetism of the nano particles have been identified as the phase state, the crystallization ratio and the core radius of the nano particles. The cause is due to the effect ferromagnetic occurs in core/shell layer of nanoparticles iron.

- The curie temperature of ferromagnetic nanoparticles in amorphous state is 1,148.9 K, crystalline state is 1,105.2 K. results are consistent with experimental results is 1,044 K [1].

- The main cause for this is the size effect caused. When the temperature of the model increases leads to the radius, the energy increases and reduce the density of the atoms (molecules) do appearance crystalline state. When the nanoparticle core radius, the crystallization process increasing leads to magnetization decrease and curie temperature increases.

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