The Effect of Vacancy Defect and size on the double perovskite Sr_2VMoO_6: A Monte Carlo study

M. El Yadari[a,b] L. Bahmad[b,*], A. El Kenz[b] and A. Benyoussef[b]

[a] *Department of Science, Moulay Ismael University, Faculté Polydisciplinaire, B.P. : 509 Boutalamine 52000 Errachidia Morocco*

[b] *Laboratoire de Magnétisme et Physique des Hautes Energies L.M.P.H.E .URAC 12 , Université Mohammed V-Agdal, Faculté des Sciences, B.P. 1014, Rabat, Morocco*

[*] *Corresponding author: bahmad@fsr.ac.ma*

Abstract: In this work, Monte Carlo simulations are performed to study the effect of vacancy defects on magnetic properties of a double perovskite Sr_2VMoO_6 film. The ions Mo^{5+} are modelized by $\sigma = 1/2$ spins, whereas the ions V^{3+} are represented by S=1 spins. The vacancy concentration and the temperature effects are examined on the behavior of the magnetizations and susceptibilities for several system sizes. From the obtained results, it is found that the increase of the defect concentration, decreases the magnitude of the magnetization, for a fixed system size. Also, we have studied the influence of an external and crystal fields on the critical behavior. Additionally, the response of the magnetization to the field shows a hysterisis behavior.

Keywords: Perovskite; Magnetic defects; Monte Carlo simulations; Magnetization; Magnetic susceptibility; Hysteresis cycle.

PACS: 73.63.Fg; 77.80.B-; 71.70.Gm; 34.20.Gj.; 81.16.Ta

I. Introduction

Physicists, chemists and material scientists have shown great interest in the **perovskite** system, because of the properties such as colossal magne- toresistance [1], half-metallicity [2], high magnetic ordering temperature [3] and magnetodielectricity [4]. These properties make them fascinating from a fundamental perspective as well as an application point of view.

The crystal structure of Sr_2VMoO_6 is that of the undistorted cubic perovskite (space group Pm-3m, a= 3.91581$\pm$ 3 $\acute{A}$), in agreement with data in Ref. [5] obtained by conventional X-ray powder diffraction.

Considering the difficulty of measurement of nano-perovskite compound Sr_2VMoO_6, especially in low tempereture, the simulation of the magnetic properties is concerned. It fills the shortage of magnetic parameters of non-perovkite compound Sr_2VMoO_6 , and point out the variation of magnetic properties with the temperature. Thus, computer simulations using the Metropolis algorithm and Monte Carlo techniques were constructed to model the behavior of several of magnetic systems. Among the systems modeled were thin films, super-lattices and double perovskite system [6, 8]. The effect of a surface magnetic field is studied by using the mean field theory (MFT) and the Monte Carlo (MC) simulations [9,10].

On the other hand, inclusion with defect, the system becomes a novel artificial structure with interesting properties. Indeed, the vacancy defects is a key factor to control the magnetic critical properties and is a new medium for exploring novel magnetic phenomena and may lead to innovative industrial applications. However, it is also known that under the normal condition, vacancy defects in material frequently occur during the material processing. As a result, the magnetic properties of the material are altered from its ideal condition and any calculation based on this ideal condition will

lead to an incorrect application design. Because of the smaller number of neighboring atomic sites, there is a reduction in the average ferromagnetic exchange coupling. As a result, this defect can be used to control the magnetic phase transition and hence the Curie temperature. The observed room-temperature ferromagnetism is believed to come from the defects [11].

For these reasons that, the magnetic thin films and multilayers have gained increasing interest for fundamental research and technological applications. The critical behavior of the spin Ising thin films has been extensively studied [12–16]. The interesting results for these systems are the dependence of the critical behavior on the thickness. It was found that the Curie temperature and the average magnetic moment per atom increase with the thickness. Wiatrowski [17] has studied the magnetic properties of thin film in a mixed-spin surface Ising model and he has shown that this simplified model gave results in quite reasonable agreement with those obtained in the most sophisticated experimental measurements of depth profile magnetization using in situ conversion electron Mossbauer spectroscopy (CEMS) on Fe(110) surfaces and thin films [18,19].

Consequently, there comes an interest to model how the vacancy defect affects the properties of the magnetic materials. It is interesting to investigate how the defect alters the magnetic behavior. In this study, the magnetic system in a reduced structure, i.e., multilayers were considered in order to investigate the magnetic profiles and its phase transition under the influence of vacancy defects, crystal field and an external magnetic field by means of Monte Carlo simulations.

II. Theoretical model

A schematic picture of the multilayer of the double perovskite system Sr_2VMoO_6 in question is presented in the Fig. 1. The multilayer system consists of a set of layers. Each layer is constituted with a square made up with LxL spins σ-layers and S-layers in the x-y direction. Whereas the number of layers are counted in the z-direction.

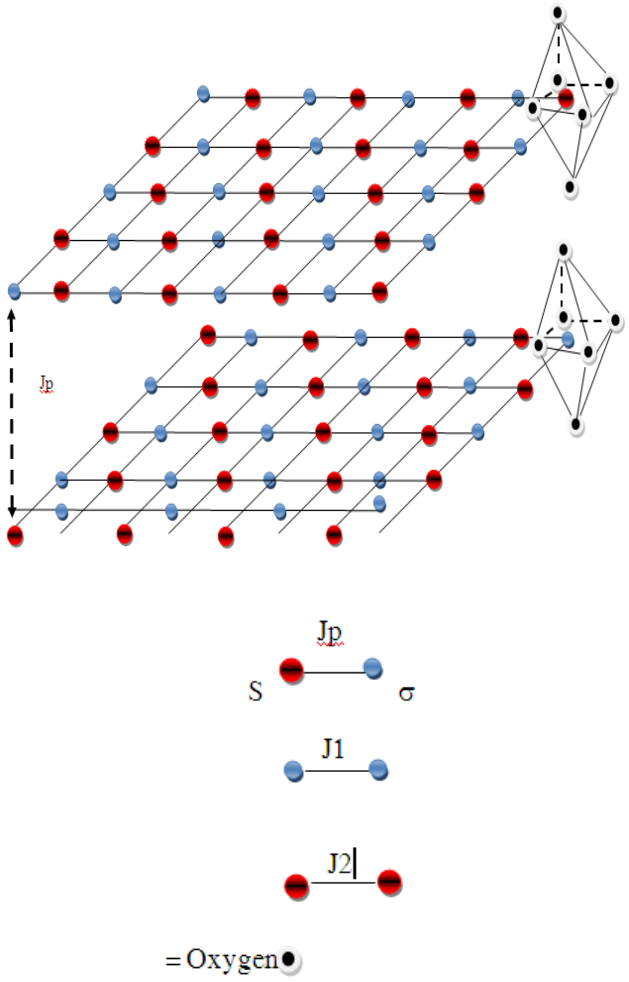


Fig. 1: A schematic view of the bilayer composed of two layers of the studied system formed with two double perovskite Sr_2VMoO_6 blocs. In all this work, the ions Mo^{5+} will be schematized by spins $\sigma = \frac{1}{2}$, whereas the ions V^{3+} will be schematized by spins S=1. The Sr atoms are not presented in this figure since these atoms are non magnetic. The constant coupling between the spins σ and σ is denoted by J_1, between the spins S and S is denoted by J_2, while J_P denotes the constant coupling between the two blocs: σ and S.

The V^{3+} (S=1) magnetic ions are located on the sub-lattice (I), while the Mo^{5+} ($\sigma = \frac{1}{2}$) magnetic ions are located on the sub-lattice (II). The first nearest neighbor of V^{3+} ions are Mo^{5+} ions, and vice versa (see Fig. 1).

The Hamiltonian of the multilayer can be written in the form of :

$$H = H_1 + H_2 + H_p + H_f \quad (1)$$

where,

$$H_1 = -J_1 \sum_{k=1}^{N} \sum_{\substack{<ij> \\ i,j \in (k)}} (\varepsilon_i \sigma_i)(\varepsilon_j \sigma_j)$$

$$H_2 = -J_2 \sum_{k=1}^{N} \sum_{\substack{<ij> \\ i,j \in (k)}} (\varepsilon_i S_i)(\varepsilon_j S_j)$$

$$H_p = -J_p \sum_{k=1}^{N} \sum_{\substack{<ij> \\ i \in (k) \\ j \in (k+1)}} (\varepsilon_i \sigma_i)(\varepsilon_i S_j)$$

$$H_f = -h \sum_{k=1}^{N} \left(\sum_j \varepsilon_j \sigma_j + \sum_i \varepsilon_i S_i \right) - \Delta \sum_{k=1}^{N} \sum_i (\varepsilon_i S_i)^2$$

where the spins *Si and* σ_i took on the values 0,±1 and $\pm \frac{1}{2}$, respectively and the sum included only first pairs nearest-neighbor. The defects correspond to $\varepsilon_i = 0$, while a magnetic site with σ_i or S_i moment correspond to $\varepsilon_i = 1$. J_1 is the constant coupling between the spins σ, whereas J_2 is the coupling constant between the spins S. J_p denotes the coupling constant between the spins σ and S. The crystal field Δ is applied only on the spins *S*, whereas the external magnetic field h is acting over all the spins σ and S.

In all this work, the coupling constants are fixed at the values: $J_1=J_2=J_P=+1$ K.

III. Monte Carlo simulations

We applied the Monte Carlo simulations under Metropolis algorithm for standard sampling method to simulate the Hamiltonian given by Eq.(1). Free boundary conditions were used in this system formed with a set of 'nlayer' layers. The simulations were performed for nlayer varying from 2,4,…,8 of the square lattice with number of atomic sites N =nlayer x L x L. Preliminary results were carried out for several system sizes: L=15, 19,…,33. Since by varying values of L does not affect the physical quantities we calculate, thus we will take L=19 spins. The vacancy concentration c, indicating the magnitude of porosity, was varied from 0 to 15 percent of N. These non-magnetic sites, being equivalent to the vacancy-type defect, do not occupy the magnetic moment, i.e., Si = 0 or $\sigma_i = 0$, giving no contribution to the above Hamiltonian.

The flips are accepted or rejected according to a heat-bath algorithm. Starting from different initial conditions, we perform 10^5 Monte Carlo steps (MCS) for each spin configuration, and discarding the first 10^4 generated configurations. We average over many configurations for each initial condition. Our programs calculate the following parameters, namely:

The internal energy per site:

$$E_T = \frac{1}{N} < H > \quad (2)$$

The magnetizations per site:

$$M_\sigma = < \frac{2}{N} \sum_i \sigma_i > \quad (3)$$

$$M_S = < \frac{2}{N} \sum_i S_i > \quad (4)$$

The corresponding total magnetization is:

$$M_{tot} = \frac{M_\sigma + M_S}{2} \quad (5)$$

The magnetic susceptibilities are given by:

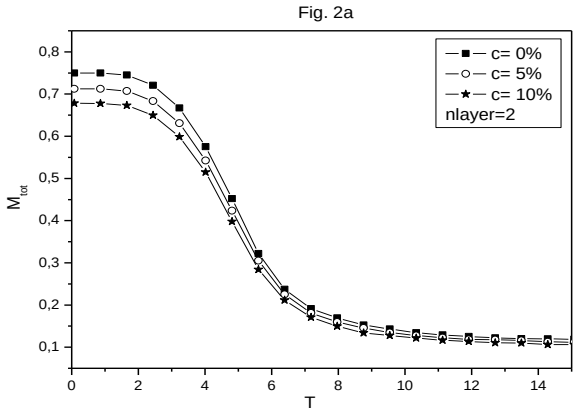
$$\chi_\sigma = \beta(< M_\sigma^2 > - < M_\sigma >^2) \quad (6)$$

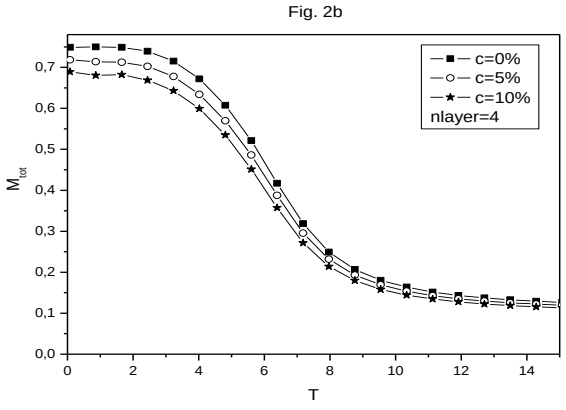
$$\chi_S = \beta(< M_S^2 > - < M_S >^2) \quad (7)$$

Where $\beta = \frac{1}{k_\beta T}$, and k_β is the Boltzmann constant. We take $k_\beta = 1$ in all the following.

IV. Results and discussions

From total magnetization M_{tot} profile for various vacancy concentration c and the number of layers nlayer, we found that with increasing the vacancy concentration c the total magnetization decreases (see Fig2 a-c). Then, the increase of vacancy concentration reduces the magnitude of the magnetic exchange coupling in the systems, and this strongly reduces the magnitude of the magnetization. Because of the smaller number of neighboring atomic sites, there is a reduction in the average ferromagnetic exchange coupling.





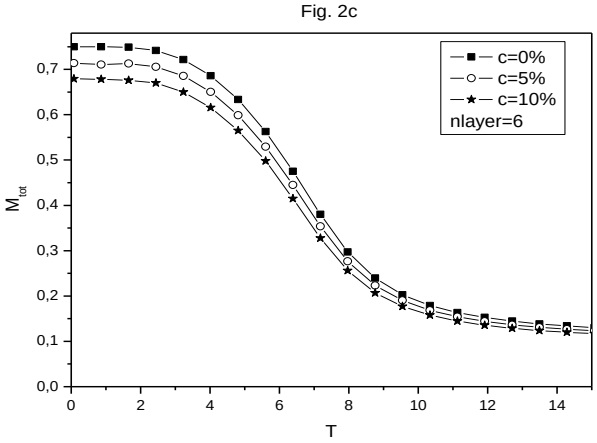


Fig. 2: The variation of magnetization as a function of temperature T, with varying the concentration from c= 0.00 to *c* = 0.15 and for a fixed value of the number of layers. (a): nlayer=2 and (b): nlayer=4 (c) nlayer=6.

Figures 3 shows the behavior of the total susceptibilities for specific system sizes: nlayer=2, 4 and 6 and for an unchanged defect concentration. The susceptibilities as a function of the temperature manifest a sharp peak. This means that the double perovskite compound approaches its critical temperature. In particular, it is found that these magnetic susceptibilities peaks are shifted to higher temperatures, when increasing the number of layers.

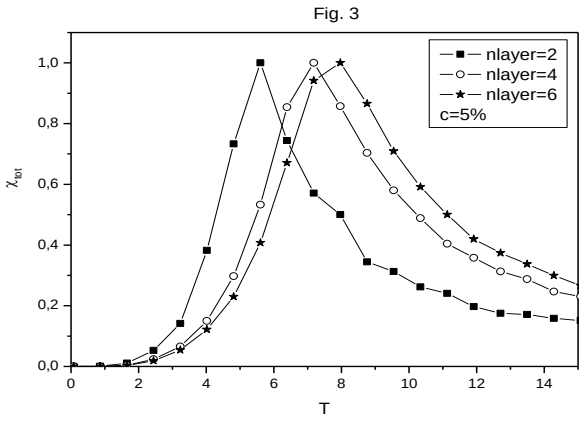


Fig. 3: The total magnetic susceptibility χ_{tot} as a function of temperature, which present an increasing of the phase transition point with varying the number of layers from nlayer = 2

to nlayer =6. For a fixed value of the concentration c=5 %.

For very low temperatures, the saturation magnetizations for the Mo^{5+} ions as well as for V^{3+} ions of the Sr2VMoO6, are 0.5 and 1, respectively [20,21]. This is in good agreement with the ground state phase diagram, in which these values are exactly: S=1 for the V^{3+} magnetic ions and for the Mo^{5+} magnetic ions.

Fig. 4

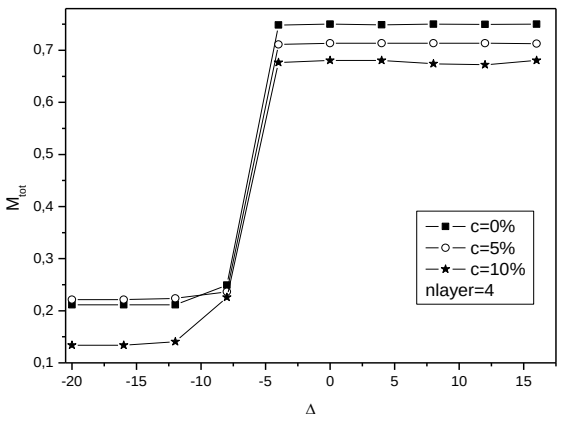


Fig. 4: The variation of total magnetization M_{tot} vs crystal field Δ. For a fixed value of nlayer=4, with varying the concentration from c= 0.00 to *c* = 0.15.

We plot in Fig. 4, the dependence of the total magnetization as a function of the crystal-field interaction for different values of the vacancy defect and for a fixed thickness. It is seen, that the total magnetization increases from a small values around 0.2 at a strong negative value of the crystal field to reach saturation ones for large positive values of the crystal field. It is observed that, these saturation values decrease with increasing the vacancy defect in the system.

An interesting behavior is seen in Fig. 5, because a great deal of information can be pointed out about the magnetic properties of a material by studying its hysteresis loop. Thus, the corresponding hysteresis loop example is shown in Fig. 5. We present the dependence of hysteresis loops on sizes keeping the values of the temperature T=1K and vacancy defect unchanged. From these results, one can see that by varying the sizes the form of the hysteresis loop changes. Therefore, the remanent magnetization and coercive field undergo modifications.

Fig. 5

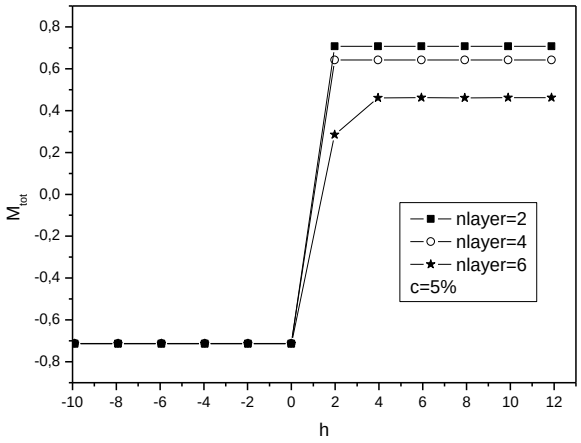


Fig. 5: Magnetization hysteresis loops for vacancy defect c=5% and temperature T=1k, with varying the number of size from nlayer=2 to nlayer=6.

We observed the decrease of the remanent magnetization which means the demagnetization. The demagnetization and coercive field increase with the increase of the layer number.

The results of the critical temperature are presented in Fig.6 as a function of the effective thickness, for two values of vacancy defect c=5% and c=15%. Then, the more vacancies, the transition from the ferromagnetic to the paramagnetic phase does not require as much thermal energy as it does for the smaller value of defect. This is because the number of vacancy sites has a strong effect on the averaged exchange coupling among the spins in the systems. Also, as can be seen in Fig.6, a linear relation between effective thickness and critical temperature is found. Then, the critical temperature increases with increasing the number of layers (thickness).

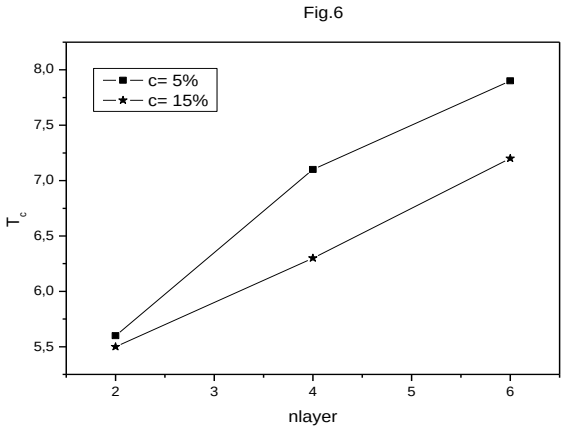


Fig. 6: The critical temperatures T_C as a function of effective thickness extracted from Monte Carlo simulations, for two values of vacancy defect c=5% and c=15%.

V. Conclusion

Monte Carlo studies on the double perovskite Sr_2VMoO_6 system were performed to investigate the effect of vacancy defect and sizes, on the magnetic properties, i.e., the magnetization and the susceptibility per spin including its critical behavior in terms of the critical temperature. However, with large number of the vacancy concentration c, we deduced that this strongly reduces the magnitude of the magnetization and the transition from the ferromagnetic to the paramagnetic phase does not require as much thermal energy as it does for the smaller value of defect. Also, this study showed that the size (thikness) of the double perovskit effects on these properties: The magnetizations versus temperature for various sizes are investigated in this system. Furthermore, the variation of the total magnetization versus crystal field is also obtained for different concentration of vacancy defect. Finally, the hysteresis loops are established for different sizes.

References

[1] S. Jin, T.H. Teifel, M. McCormack, R.A. Fastacht, R. Ramesh, L.H. Chen, Science 254 (1994) 413.

[2] K.I. Kobayashi, T. Kimura, H. Saeada, K. Tekura, Y. Tokura, Nature 395 (1988) 677.

[3] B. Garcia-Landa, C. Ritter, M.R. Ibarra, J. Blasco, P.A. Algarabel, R. Mahendiran, J. Garcia, Solid State Commun. 110 (1999) 435.

[4] C. Zhong, J. Fang, Q. Jiang, J. Phys: Condens. Matter 16 (2005) 9059.

[5] V.A. Fotiev, G.V. Bazuev, V.G. Zubkov, Izv. Akad. Nauk SSSR, Neorg. Mater. 23 (1987) 1005–1008.

[6] H. Jeong, B. Kahng, S. Lee, C.Y. Kwak, A.-L. Barabási, J.K. Furdyna *Physical Review E* 65, 031602 (2002).

[7] M. El Yadari, L. Bahmad, A. El Kenz, A. Benyoussef, Monte Carlo study of the double perovskite nano Sr2VMoO6, (2013), doi: http://dx.doi.org/10.1016/j.jallcom.2013.01.158

[8] M. El Yadari, L. Bahmad, A. El Kenz, A. Benyoussef, Physica A 392 (2013) 673–679.

[9] L. Bahmad, A. Benyoussef, H. Ez-Zahraouy, Physical Review E 66 (2002) 056117.

[10] L. Bahmad, A. Benyoussef, Physica Status Solidi B 243 (2006) 1939.

[11**]** Y. Wang, Y. Huang, Y. Song, X. Zhang, Y. Ma, J. Liang, and Y. Chen, Nano Lett., **9** (2009) 220.

[12] A. Moutie, M. Kerouad, J. Magn. Magn. Mater. 238 (2002) 233.

[13] Y. EL Amraoui, A. Khmou, J. Magn. Magn. Mater. 218 (2000) 182.

[14] J.W. Tucker, J. Magn. Magn. Mater. 210 (2000) 383.

[15] T. Kaneyoshi, Physica A 349 (2005) 183.

[16] J. Mazo-Zuluaga, J. Restrepo, Physica B 384 (2006) 224.

[17] G. Wiatrowski, J. Magn. Magn. Mater. 136 (1994) 209.

[18] J. Korecki, U. Gradmann, Hyperfine Iteractins 28 (1984) 3207.

[19] J. Tyson, A.H. Owens, J.C. Walker, G.J. Bayerenther, Appl. Phys. 52 (1981) 2487.

[20] D. D. SARMA and SUGATA RAY, Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 113, Nos 5& 6, October–December 2001, pp 515–525.

[21] P. Karen , A.R. Moodenbaugh, J. Goldberger, P.N. Santhosh, P.M. Woodward, Journal of Solid State Chemistry 179 (2006) 2120 – 2125.

