
Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Montecarlo Simulation of Intercalated Atomic Distributions in Layered Dichalcogenide

Saiko Negishi [a], Hiroshi Negishi [a], Minoru Sasaki [a] & Masasi Inoue [a]

[a] Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima, 739-8526, Japan

Version of record first published: 27 Oct 2006

To cite this article: Saiko Negishi, Hiroshi Negishi, Minoru Sasaki & Masasi Inoue (2000): Montecarlo Simulation of Intercalated Atomic Distributions in Layered Dichalcogenide, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 69-74

To link to this article: http://dx.doi.org/10.1080/10587250008026119

*Mol. Cryst. and Liq. Cryst.*, 2000, Vol. 341, pp. 69-74
Reprints available directly from the publisher
Photocopying permitted by license only





# MonteCarlo Simulation of Intercalated Atomic Distributions in Layered Dichalcogenide

SAIKO NEGISHI, HIROSHI NEGISHI, MINORU SASAKI
and MASASI INOUE

*Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima 739–8526, Japan*

Atomic distributions of intercalated guest atoms into layered dichalcogenide have been simulated taking into account the interactions between the first and second nearest neighboring guest atoms in the triangular lattices stacked with 6 layers (lattice size $18 \times 18 \times 6$) using a MonteCarlo method. With these distributions, the X-ray patterns of $Fe_xTiS_2$ with $x = 0.25$ having the $2\sqrt{3}a \times 2a \times 2c$ superlattice with the fractional site occupancy have been reproduced qualitatively by averaging the intensities for different patterns obtained by different random seeds.

*Keywords:* MonteCarlo simulation; atomic distribution; dichalcogenide

## INTRODUCTION

Intercalation of guest atoms, such as 3d transition metals M, into a host layered dichalcogenide produces intercalation compounds with a variety of interesting structural, electrical, and magnetic properties depending on the kind of the guest atoms and their concentration $x$ [1, 2]. Among others, Fe intercalates of $TiS_2$, $Fe_xTiS_2$, show spin-glass (SG, $0.01 \leq x \leq 0.20$), cluster-glass (CG, $0.20 < x \leq 0.40$), and ferromagnetic phases (F, $x > 0.40$) [3]. Thus far we have studied the relaxation phenomena of thermoremanent magnetizations $M_r$ of SG and CG phases using an anomalous Hall effect and analyzed the observed time decay curves of $M_r$ based on a domain theory, which shows that these materials have very broad equilibrium relaxation spectra, suggesting an important role of the distributions of the guest Fe atoms, or the formation of some clusters [4, 5].

On the other hand, the X-ray diffraction for single crystals of $Fe_xTiS_2$ [6] and neutron powder diffraction patterns [7] reveal the formation of the $2\sqrt{3}a \times 2a \times 2c$ superlattice for $x = 0.25$ and $\sqrt{3}a \times \sqrt{3}a \times 2c$ for $x = 1/3$ with some

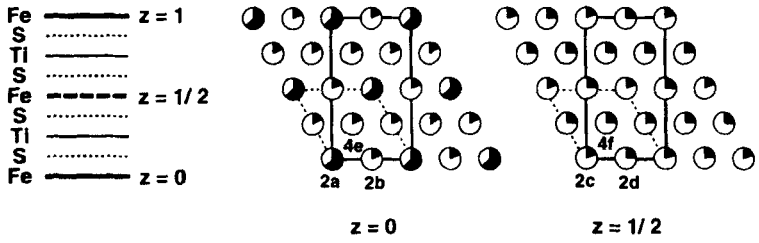


FIGURE 1 Arrangements of Fe atoms in the $2\sqrt{3}a \times 2a \times 2c$ superlattice for $Fe_xTiS_2$ with $x = 0.25$ by Kuroiwa *et al.*[6, 7] Fan-shaped black area indicates the fractional site occupancy of the 2a, 2b and 4e sites at $z = 0$, and 2c, 2d and 4f sites at $z = 1/2$. The unit cells in planes are indicated by solid lines. For comparison, the unit cells in the $2a \times 2a \times 2c$ superlattice are indicated by broken lines.

fractional site occupancy at the Fe sites less than unity, as shown for the case of $x = 0.25$ in Fig. 1, where $a$ and $c$ are the lattice constants of the host $TiS_2$. The occupancies of the 2a, 2b and 4e sites at $z = 0$, and 2c, 2d and 4f sites at $z = 1/2$ are determined to be 0.63(10), 0.19(5), 0.18(2), 0.20(1), 0.25 (5) and 0.25(3), respectively, from the analyses by the Rietvelt profile-fitting method. Since the occupancies of the 2b and 4e sites and those of 2d and 4f sites are nearly equal, the Fe lattice has pseudo-haxagonal symmetry and forms the $2a \times 2a \times 2c$ superlattice, as indicated by broken lines in Fig. 1. In the real crystal, however, the Fe atoms may have very complicated distributions in the van der Waals gaps. In the present work, we have made computer simulations for the equilibrium distribution of intercalated guest atoms in a layered dichalcogenide using a MonteCarlo method. Here we have taken into account the interactions between the first and second nearest neighboring guest atoms in the triangular lattices stacked with six layers (lattice size: $18 \times 18 \times 6$) with the periodic boundary condition along the $a$- and $c$-axis directions.

## CALCULATION

The MonteCalro calculations have been made using the system Hamiltonian as,

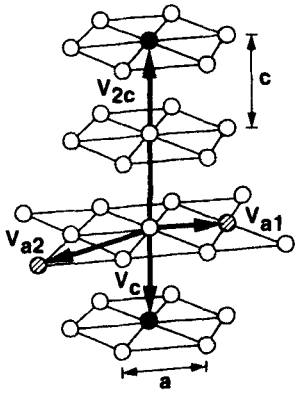


FIGURE 2 Interaction strengths between the first and second nearest neighboring guest atoms in the triangular lattices; $V_{a1}$ and $V_{a2}$ in the $a$-axis layer, and $V_c$ and $V_{2c}$ along the $c$-axis, respectively.

$$H = - \sum_{<i,j>} n_i \left( V_{a1} n_j^{a1} + V_{a2} n_j^{a2} + V_c n_j^{c} + V_{2c} n_j^{2c} \right), \qquad (1)$$

where $n_i$ (= 1 or 0) is an M occupancy of $i$-th site, $n_j^{a1}$ and $n_j^{a2}$ those of $j$-th site, $V_{a1}$ and $V_{a2}$ a pair-interaction strength between the first nearest neighbors and the second ones in the $a$-axis layer, and $n_j^{c}$, $n_j^{2c}$, $V_c$ and $V_{2c}$ the corresponding values of the guest atoms of the first and second nearest layers along the $c$-axis, respectively. The numerical calculations for $M_xTiS_2$ have been done over the whole concentration range $x$ = 0 - 1 at $T$ = 870 °C (the growth temperature of the single crystals) [1]. Using the obtained atomic distributions of Fe guests in $Fe_xTiS_2$ with $x$ = 0.25, as well as for the $2\sqrt{3}a \times 2a \times 2c$ superlattice with the fractional site occupancy, we have calculated the X-ray diffraction intensities to compare with the experiments.

## RESULTS AND DISCUSSIONS

A typical result of the calculated atomic distributions in the six consecutive layers ($m$ = 1, 2, ..., 6) for $Fe_xTiS_2$ with $x$ = 0.25 is shown in Fig. 3a, obtained with the best-fit values of the repulsive interaction strengths $V_{a1}$ = -10000 K, $V_{a2}$ = -5000 K, $Vc$ = -5000 K, and attractive strength $V_{2c}$ = + 5000 K. The Fe atoms in each layer are seen to scatter homogeneously, similar to those for $2\sqrt{3}a \times 2a$ (or $2a \times 2a$). Furthermore, we note nearly the same atomic patterns

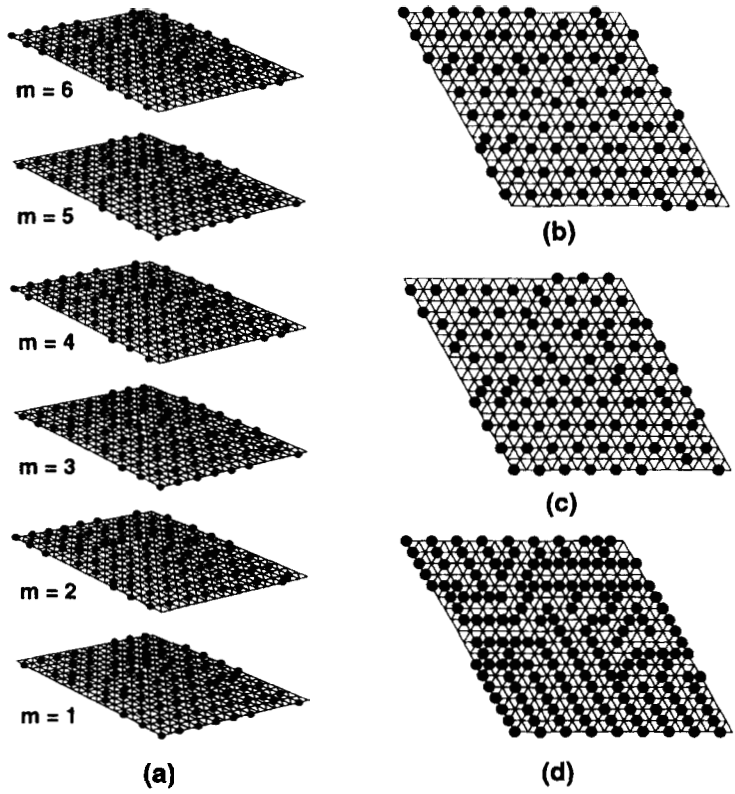


FIGURE 3 (a) Calculated atomic distributions of Fe atoms in the six consecutive layers for $Fe_xTiS_2$ with $x = 0.25$ using the best-fit values of the repulsive interaction strengths $V_{a1}$, $V_{a2}$, $V_c$, and attractive strength $V_{2c}$. (b) The projected pattern of the even number layers along the $c$-axis, and (c) that of the odd number layers. (d) The projection over all layers along the $c$-axis.

for the even ($m$ = 2, 4, 6) or odd number ($m$ = 1, 3, 5) layers, as seen from their projections along the $c$-axis, as depicted in Figs. 3b and 3c, respectively. As a result, some nearly regular pattern with the periodicity of $2c$ is formed, as illustrated in the overall projection along the c-axis direction (Fig. 3d).

We have found that the calculated distribution patterns are strongly dependent on the interaction strengths and guest concentration $x$, which are characterized by the averaged numbers of the first and second nearest

neighbors, $z_k = (\Sigma n_i n_j^k)/Nx$ with $k$ = a1, a2, c, and 2c, and total site number $N$. In the case with no interaction between the guest atoms, the atoms are distributed randomly, and $z_k$ is proportional to $x$. In the cases with attractive interaction $V_{a1}$ (> 0), guest atoms tend to gather to form some clusters, while in the case with repulsive interaction $V_{a1}$ (< 0) they are scattered over the lattice homogeneously. Correspondingly, $z_{a1}$ is increased with positive $V_{a1}$ and decreased with negative $V_{a1}$ but $z_c$ is almost unchanged by $V_{a1}$. Similarly, $V_k$ affect strongly on the averaged number $z_k$. For the cases with more than two kinds of $V_k$, the situation becomes more complicated due to some cooperation and/or competition between the interaction strengths.

With these obtained atomic distributions, we have calculated the X-ray intensities of $Fe_xTiS_2$ with $x$ = 0.25 for ($\xi$, 1/2, 1/2) along the $a^*$-axis and (0, 1/2, $\zeta$) along the $c^*$-axis. We should note that the calculated X-ray intensities of ($\xi$, 1/2, 1/2) and (0, 1/2, $\zeta$) from a single pattern of 18 × 18 × 6 lattice

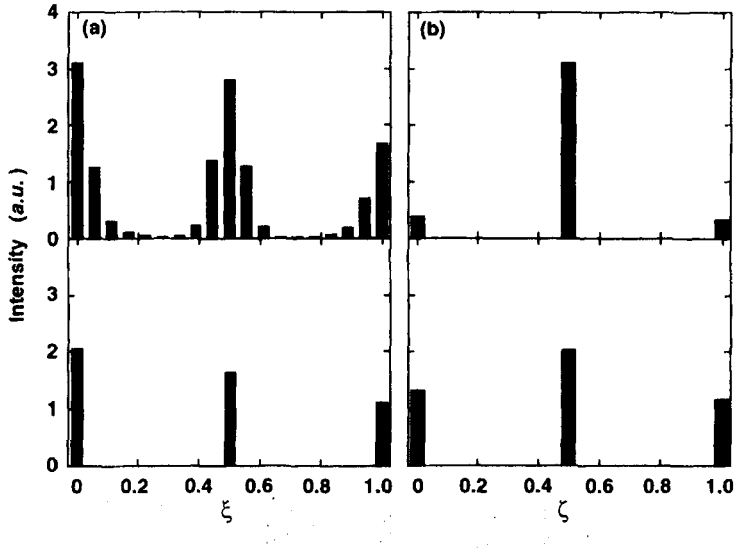


FIGURE 4 The calculated X-ray intensities of (a) ($\xi$, 1/2, 1/2) along the $a^*$-axis and (b) (0, 1/2, $\zeta$) along the $c^*$-axis for $Fe_xTiS_2$ with $x$ = 0.25. Upper parts illustrate the averaged intensities for ten patterns obtained by different random seeds, and lower parts the patterns for the $2\sqrt{3}a \times 2a \times 2c$ superlattice with the fractional site occupancy in Fig. 1.

depend strongly on the 'random seeds' used, which means that the lattice size $18 \times 18 \times 6$ we employed may be too small to reproduce the structural details in the real system. Therefore, we have taken the averaged intensities for ten patterns obtained by different random seeds. The results of ($\xi$, 1/2, 1/2) and (0, 1/2, $\zeta$) are illustrated in upper parts of Figs. 4a and 4b, respectively, which are in qualitative agreement with the patterns for the $2\sqrt{3}a \times 2a \times 2c$ superlattice with the fractional site occupancy (lower parts). These results indicate that the real atomic distribution for $Fe_xTiS_2$ with $x = 0.25$ can be considered as an assemblage of the atomic patterns randomly scattered, each of which has nearly $2\sqrt{3}a \times 2a \times 2c$ local structure, as shown by the simulations using the small lattice size $18 \times 18 \times 6$. In other words, there exists a rather large randomness in the real system, and the ensemble average is important in the calculations to reproduce the essence of the superlattice with the fractional site occupancy observed experimentally.

**Acknowledgements**

The authors thank Prof. Y. Kuroiwa for giving us the detailed experimental data of $Fe_xTiS_2$ and valuable discussion, and M. Sakamoto for his help in making part of the computer programs used in this work.

## *References*

[1] M. Inoue, H.P. Hughes and A. D. Yoffe, *Adv. Phys.*, **38,** 565 (1989).
[2] M. Inoue and H. Negishi, in *Recent Advances in Magnetism of Transition Metal Compounds*, edited by A. Kotani and N. Suzuki (World Scientific Pub., Singapore, 1993), p. 193.
[3] H. Negishi, A. Shoube, H. Takahashi, Y. Ueda, M. Sasaki, and M. Inoue, *J. Magn. Magn. Mater.*, **67,** 179 (1987).
[4] Y. Hara, H. Negishi, M. Sasaki and M. Inoue, *J. Magn. Magn. Mater.*, **159,** 125 (1996).
[5] H. Negishi, A. Yamasaki, M. Sasaki, M. Inoue, and H. Kadomatsu, *J. Magn. Magn. Mater.*, **185,** 85 (1998).
[6] Y. Kuroiwa, M. Nishimura, R. Nakajima, H. Abe and Y. Noda, *J. Phys. Soc. Japan*, **63,** 4278 (1994).
[7] Y. Kuroiwa, M. Nishimura, Y. Noda and Y. Morii, *Physica B*, **213&214,** 396 (1995).