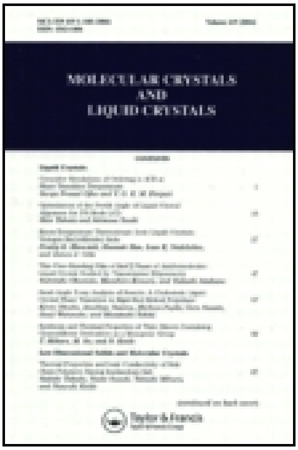

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MONTE CARLO SIMULATION ON SHORT TO LONG RANGE ORDERING IN Li_xTiSe_2

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Abstract

Monte-Carlo simulations of lithium ordering are presented allowing to determine Li-Li interactions from reproduction of the ^{77}Se NMR lines and of the titration curve of the Li/$TiSe_2$ system. It is shown that one has to account for interaction up to the third neighbor for $x > 0.5$ content.This is related to the percolation threshold of the electronic screening of the ions. Diffraction patterns simulated from the ion distributions show occurrence of long range ordering for lithium content beyond 0.50.

INTRODUCTION

Lithium ordering in lamellar dichalocogenides was first evidenced in the LixTiS2 system from electrochemical potential spectroscopy[1]. In the selenides compounds this ordering was observed through ^{77}Se NMR studies, first in the $Li_xZrSe_{1.95}$ system[2], then in the Li_xTiSe_2 one[3]. At low temperature, when the Li^+ ions are immobile at the time scale of the hyperfine interaction of the Li^+ electronic screen with the ^{77}Se nuclei, the NMR spectra are resolved in four components corresponding to Se nuclei experiencing various Li^+ environnements, mainly 0, 1, 2 or 3 Li^+ in the first neighbour sites of the van der Waals intercalation gap (figure 1). Monte-Carlo simulations of the lithium distributions was done previously, taking into account first-neighbor Li^+-Li^+ interaction only[2]. It reproduced quite well these NMR spectra and the shape of the titration curve but for low Li amounts only, mainly giving evidence for a strong local ordering for x=1/3 and also for x=0.5 . Here, in the Monte-Carlo simulations, we introduce Li-Li interactions up to the third neighbor in order to reproduce the behavior of the system for large intercalation contents.

MONTE CARLO MODELING FOR Li^+- Li^+ INTERACTIONS

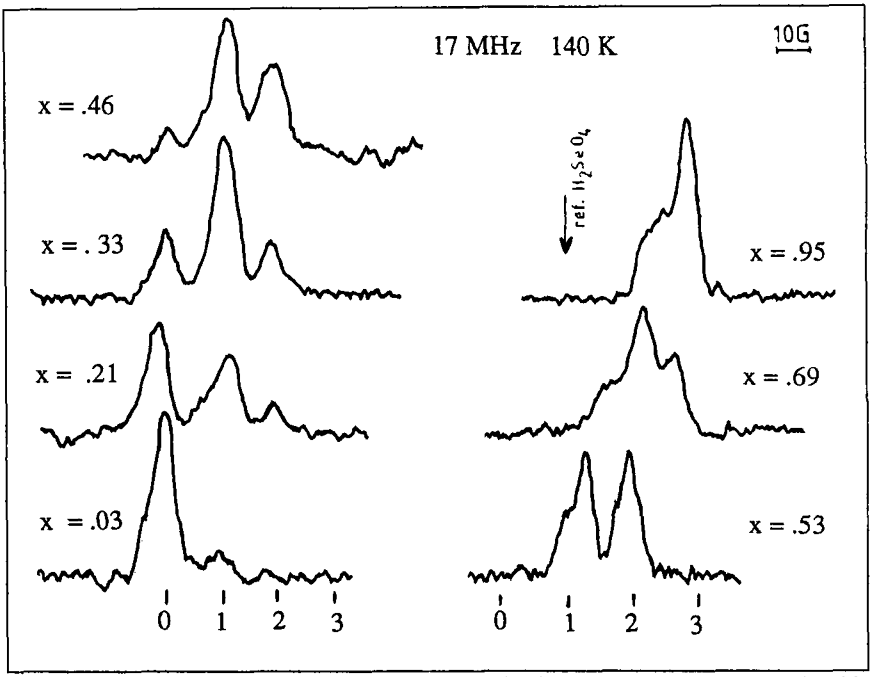

Figure 1 ^{77}Se low temperature NMR spectra of Li_xTiSe_2 (0.03 < x 0.95) obtained by Fourier transform of the dipolar echos at 500µS. 0, 1, 2, 3 indicate the line components corresponding to Se atoms having 0, 1, 2 or 3 first lithium neighbors.

This simulation was limited to the dimension two, because of the very weak interactions between the lithium ions on each side of the slabs (no stage compounds are observed in the Li-MX_2 systems (X = S, Se)).

The first Monte Carlo simulation step consists in a random throw in a n x n triangular lattice with periodic limit conditions. Each node of that lattice corresponds to an octahedral site of the Van der Waals gap and can accommodate a lithium ion. Then a thermal relaxation of the Boltzmann type was introduced allowing lithium to jump to an available empty site, possibly by minimizing the energy of the system. The potential can be written :

$$V(x) = V_0 - U(x) - \frac{\eta kt}{e} Ln\frac{x}{1-x} \quad (1)$$

with : η : entropic prefactor, k : Boltzmann constant, x : intercalation amount
T : temperature, U(x) : interaction term.

Instead of following a linear variation as a function of lithium content, we use an interaction term which does not relate to the hypothesis of a mean field[4]. It only depends on the energy of each site which is correlated to the lithium environment of this site. The global interaction term is obtained by summation over the lattice as follow :

$$U(x) = \frac{\sum_k Li(k) E_l(k)}{n^2 x} \tag{2}$$

with n : dimension of the simulated square, x: intercalation content

$E_l(k)$: energy contribution for k first neighbors for a given lithium ion

$Li(k)$: number of lithium ions surrounded by k first lithium neighbors.

By replacing this interaction energy in equation (1), one can obtain the comparison between the real potential of the Li^+/Li_xTiSe_2 couple and its simulated value.

After each lithium content increment and following thermal relaxation, the ^{77}Se environment is calculated in order to simulate the NMR line shape.

Contribution to one lithium site energy ($E_l(k)$) are tested until both the simulated NMR line shape and the Li^+/Li_xTiSe_2 potential versus lithium composition correspond to the observed values.

RESULTS

First Li^+-Li^+ neighbor interactions

The Li_xTiSe_2 potential simulation was obtained by taking into account only the first lithium neighbor interaction (as mentionned above) and is in good agreement with the observed one. The contribution to the energy of one lithium site is given in table I.

Table I lithium site energy contribution as a function of Li^+ environment

k	0	1	2	3	4	5	6
$E_l(k)$ (meV)	0	5	20	45	80	125	180

The calculated intensities of the NMR ^{77}Se lines were obtained with the same conditions (Table II) and show that if the agreement is very good for the concentrations corresponding to x = 0.33 and 0.53, it is not the case for x = 0.69.

Second and third Li^+-Li^+ neighbor interactions

It was then necessary to take into account the interaction energy between second and third neighbor lithium ions to correctly simulate the Li_xTiSe_2 intercalates[5].

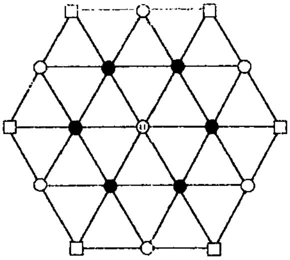

Figure 2 First (●), second (○) and third (□) lithium sites in an octahedra 2D plane.

Table II Observed and simulated ^{77}Se NMR line components intensities for first* only and second and third** neighbor Li^+-Li^+ interactions.

lithium content		Se(0) (%)	Se(1) (%)	Se(2) (%)	Se(3) (%)
0.33	experimental	18	61	21	-
	simulated*	18	64	18	-
	simulated**	21	58	20	1
0.53	experimental	ε	52	48	-
	simulated*	1.8	47.8	48.8	1.5
	simulated**	6	43	47	4
0.69	experimental	0	20	48	32
	simulated*	0	10	80	10
	simulated**	4	18	46	32

Figure 2 shows one lithium environment and table III indicates the new contribution values to the energy of a lithium site.

Table III lithium site energy contribution as a function of Li^+ environment

k	1	2	3	4	5	6
$E_1(k)$ (meV)	6	24	54	76	90	100
$E_2(k)$ (meV)	1	3	11	25	50	90
$E_3(k)$ (meV)	0	2	8	20	40	65

Table II summarizes the results concerning NMR lines intensities obtained under this new condition. Figure 3a, b, c clearly pictures the local order of $a.\sqrt{3}.a\sqrt{3}$ for $Li_{0.33}TiSe_2$, that of $a.a\sqrt{3}$ for $Li_{0.53}TiSe_2$, and the absence of order for $Li_{0.69}TiSe_2$. With these new parameters, both the ^{77}Se NMR shape and the calculated potential are correctly simulated .The necessity to introduce interaction to second and third neighbor to correctly simulate $Li_{0.69}TiSe_2$, hints to a change in the electronic properties of the system because of lithium electronic screening percolation. As in the case of the Li-$ZrSe_y$ (y>1.90), these results indicate a strong ion/electron coupling in the intercalates.

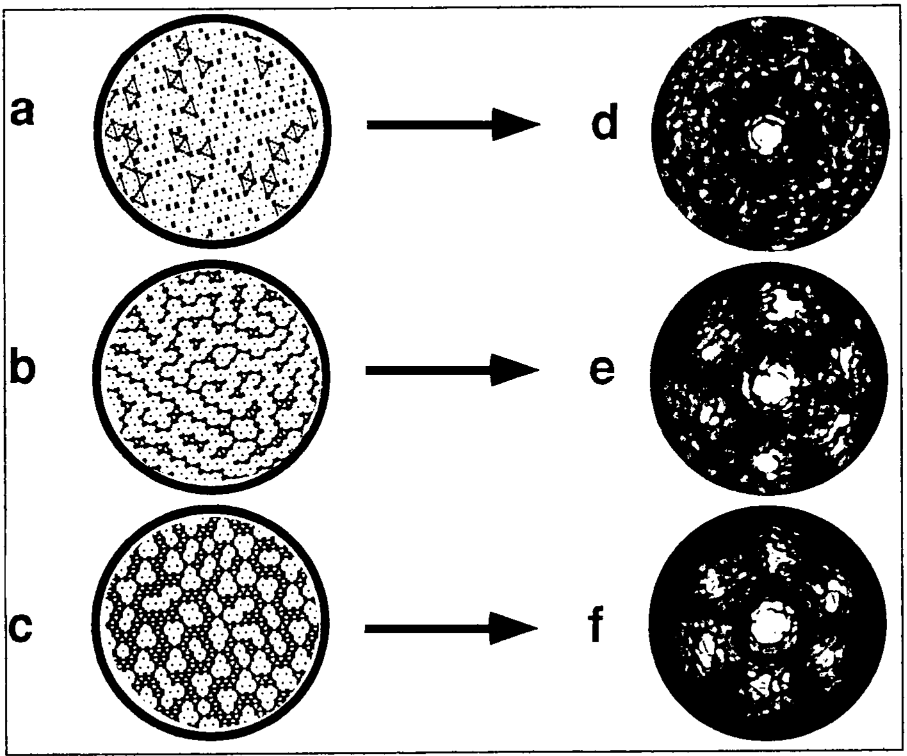

Figure 3 a ,b and c : simulations for x = 0.33, 0.53 and 0.66 respectiveley. d, e and f are corresponding diffraction patterns.

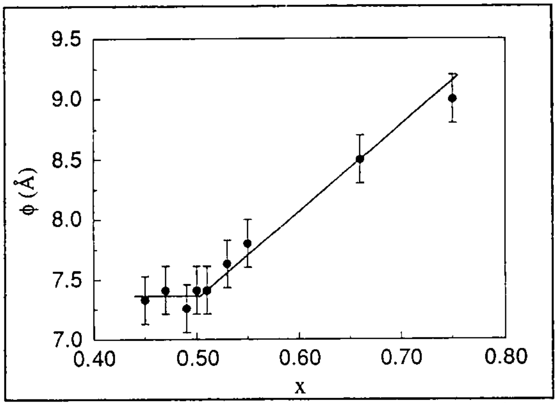

Figure 4 evolution of 2D diffracting domains with lithium content.

LONG RANGE ORDERING MANIFESTATION and CONCLUSION

To test any possible change in the ordering range beyond the percolation threshold ($x = 0.50$), we did a diffraction experiment from the 2D distribution we had simulated before. A laser beam was used to illuminate a slide of the distribution. Appropriate lens were used to focus on a Polaroïd film either the direct distribution or its image in the reciprocal space (its 2D fourier transform). Figure 3d, e, f shows the different patterns obtained as a function of lithium content. For lower x values, no diffraction spots could be seen, whereas they appeared for x = 0.50. Beyond this value, the spots size increased by coalescence while the hexagonal pattern size decreased, indicating, in particular, that the size of the 2D diffracting domains was increasing. This evolution is reported in figure 4 where the ordinate axis was calibrated using a screen with a known step as diffracting pattern. It is thus possible that below x = 0.50 the Li^+-Li^+ interaction is only a short range one explaining the good agreement between the observed data and the simulation with only the first neighbors. On the other hand, for $Li_{0.69}TiSe_2$, the percolation threshold being crossed, the Li^+-Li^+ interaction is felt at a much longer range.

In the Li_xTiSe_2 compound, the quadrupolar coupling of ^7Li as well as the NMR line shift show a linear variation versus lithium content and rules out any qualitative change in the electronic screen. However, even if the local screen does not undergo any sudden alteration, nothing allows to foresee what can happen to the long distances interactions.

In particular, whereas the Li-$ZrSe_{1.94}$ system presents a discontinuity in the cell parameters variation around x = 0.40, it is only for x = 0.50 that a change in the slope of the c parameter vs x appears in the Li_xTiSe_2 system. This value of 0.50 corresponds precisely to the crossing of the percolation threshold in this latter system if one takes into account the interactions as deduced from the Monte Carlo simulation. Then, the strong electronic localization around the intercalated lithium ions implies that, at the percolation threshold, the system goes from a semi-metallic to a metallic state. The bands overlap which was taking place only in some directions of the reciprocal lattice is occurring in all directions for x > 0.50. This preliminary results, based on the study of the diffraction pattern of the ions distribution after simulation, seem to indicate that such a tendency exists for x close to the percolation threshold.

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