The lattice gas model on tetrahedral sites of a BCC lattice: anisotropic diffusion in the intermediate phase

J. Phys. C: Solid State Phys. **19** (1986) L273–L277. Printed in Great Britain

LETTER TO THE EDITOR

The lattice gas model on tetrahedral sites of a BCC lattice: anisotropic diffusion in the intermediate phase

György Szabó† and János Kertész‡

† Central Research Institute for Physics, H-1525 Budapest, POB 49, Hungary

‡ Research Institute for Technical Physics, H-1325 Budapest, POB 76, Hungary

Received 22 February 1986

Abstract. Monte Carlo simulations were carried out on the lattice gas model of tetrahedral interstitial sites in the BCC lattice. Repulsive first- and second-neighbour interactions were explicitly taken into account whereas further ranging forces were handled via mean-field terms. Anisotropic diffusion was observed in the low-temperature ordered and in the intermediate partially ordered phase. This latter phase is a candidate for describing the anomalous properties of α-AgI.

Lattice gas models provide a useful means of describing several physical systems including super-ionic conductors, monolayers on surfaces, metal–hydrogen systems and other intercalation compounds. The problem of diffusion in lattice gases has received much interest in recent years (for a review see Kehr and Binder (1983)).

One serious drawback to this kind of approach is that the actual lattice structures are often complex and special phenomena may occur because of these peculiarities. For example in α-AgI the I^- ions build up a BCC lattice and the tetrahedral interstitial sites form the underlying lattice where the Ag^+ ions jump and on which lattice gas has to be studied. This complex structure is also characteristic of many other materials, such as Ag_2S, Ag_3SI, CuBr, NbH_x, VH_x, $PdCuH_x$ etc; thus the understanding of its consequences is very important.

The lattice gas model on this lattice was first studied by Horner and Wagner (1974) who described the 'gas–liquid' transition in HbH_x. Recently this model was extended to investigate the effect of randomly distributed substitutional impurities for hydrogen in niobium–molybdenum alloys which seems to be a realistic example of a random-field Ising model (see Shirley *et al* 1984 and references therein). However, in the above works the possibility of partially ordered states was not studied. In a recent study (Szabó 1986, hereafter referred to as I) a six-sublattice mean-field approximation with repulsive first- and second-neighbour interactions and a fixed number of particles was carried out. A large variety of phase transitions were observed as a function of the coupling constants. Interestingly, in some range of the parameters an intermediate partially ordered phase was found to be stable between the low-temperature ordered and the high-temperature disordered phases. In I one of the intermediate phases was suggested as a possible interpretation of Raman scattering (Mariotto *et al* 1981) and specific heat (Perrott and Fletcher 1969) data on α-AgI.

In this Letter we present the results on the Monte Carlo simulations of the above

model showing that self-diffusion is strongly anisotropic in the partially ordered intermediate phase as well as in the ordered low-temperature one.

The unit cell of the lattice, consisting of tetrahedral interstitial sites in a BCC lattice, is shown in figure 1 where the six-sublattice structure is indicated.

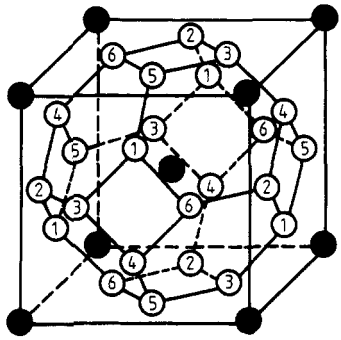

Figure 1. Tetrahedral interstitial sites (open circles) in the BCC lattice (full circles) form a non-Bravais lattice. The six-sublattice separation is indicated by the numbers 1–6 in the unit cell.

Introducing the occupation number n_i on site i we consider the following Hamiltonian:

$$E = aE_{\mathrm{L}} + (1 - a)\, E_{\mathrm{MF}} \tag{1}$$

where the local part E_{L} reads as

$$E_{\mathrm{L}} = J \sum_{\mathrm{NN}} n_i n_j + \gamma J \sum_{\mathrm{NNN}} n_i n_j. \tag{2}$$

The first summation runs over the nearest neighbours; the second one over the next-nearest neighbours with J, $\gamma > 0$ corresponding to repulsive interaction due to Coulomb force. Only the first- and second-neighbour interactions are treated locally, while the further terms are taken into account within the framework of a six-sublattice mean-field approximation:

$$E_{\mathrm{MF}} + J' \sum_{\mathrm{NN}} \bar{n}_i n_j + \gamma' J' \sum_{\mathrm{NNN}} \bar{n}_i n_j \tag{3}$$

where $\bar{n}_i$ represents the average occupation of site i which is equivalent to the corresponding sublattice occupation $\langle n \rangle_s; s = 1, \ldots, 6$ (as detailed in I). We restrict ourselves to a fixed number of particles corresponding to the composition of AgI:

$$\sum_{s=1}^{6} \langle n \rangle_s = 1. \tag{4}$$

In order to go beyond the mean-field calculations of I we have carried out Monte Carlo simulations. This method is a standard way of studying the properties of lattice gases including transport phenomena (Kehr and Binder 1983). For details on the Monte Carlo method see the review by Binder and Stauffer (1983). An $8 \times 8 \times 8$ lattice was considered with periodic boundary conditions containing 6144 lattice sites with 1024 particles using diffusion dynamics. For $a = 0$, the mean-field results of I were reproduced;

for $a = 1$, no ordering occurred corresponding to the fact that the ordered phase is caused by the farther-neighbour interactions at the given concentration. Our main aim was to investigate the differences of the transport properties in the different phases; therefore runs were carried out for three parameter values representing the ordered, the disordered and the intermediate phases. We chose $J = J' = 1$, $\gamma = \gamma' = 0.25$ and $a = 0.5$ because it is here that the intermediate phase occurs. The results obtained for the three temperature values are shown in figures 2 and 3.

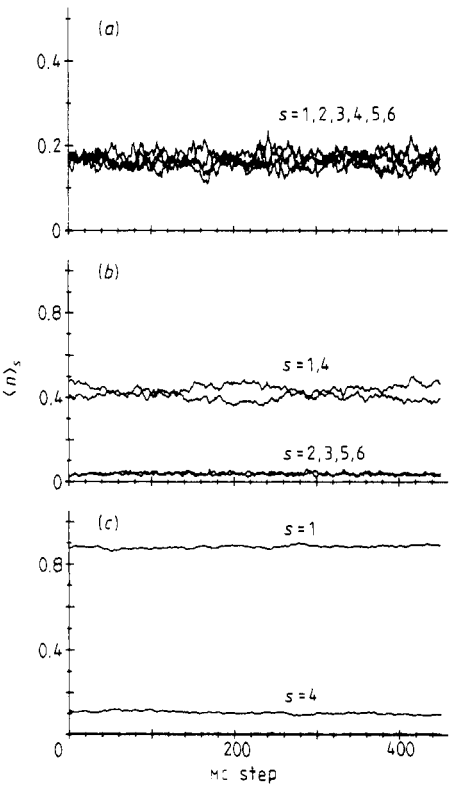

Figure 2. Sublattice occupations as a function of time in Monte Carlo steps/particle (*a*) in the high-temperature disordered phase ($k_BT/J = 0.13$); (*b*) in the partially ordered intermediate phase ($k_BT/J = 0.11$); (*c*) in the low-temperature ordered phase ($k_BT/J = 0.08$).

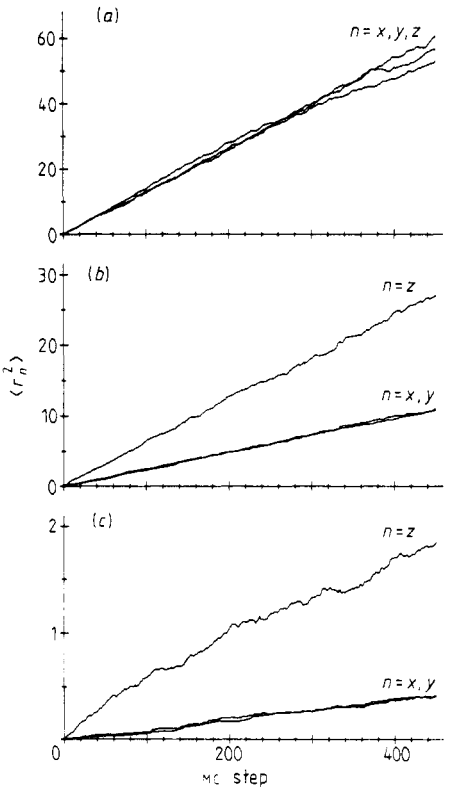

Figure 3. Mean square displacements in the x, y, z directions versus time (*a*) in the high-temperature phase; (*b*) in the intermediate phase; (*c*) in the low-temperature phase. The temperatures are the same as in figure 2.

In the disordered phase the sublattice occupations are equal (figure 2(*a*)); in the intermediate phase the particles are equally distributed on two sublattices which are connected with second-neighbour interactions whereas the other four sublattices are almost empty (figure 2(*b*)). Finally, at low temperature, in the ordered phase, particles prefer to reside on one sublattice (figure 2(*c*)) reflecting that in the ground state ($T = 0$) one of the six sublattices is fully occupied. In order to equilibrate the system several hundreds of Monte Carlo steps per particle were omitted depending on the temperature

and no transients were observed afterwards (see figure 2). No systematic size dependence was found compared with $6 \times 6 \times 6$ and $7 \times 7 \times 7$ lattices.

The results for self-diffusion are plotted in figure 3. The self-diffusion coefficients in the three coordinate directions were separately calculated as

$$D_n = \lim_{t \to \infty} \frac{1}{t} \langle \Delta r_n^2 \rangle \qquad n = x, y, z \tag{5}$$

where t is measured in Monte Carlo steps per particle and $\langle \Delta r_n^2 \rangle$ is the mean square displacement in direction n. For simplicity the lattice constant is taken to be 4. Movements crossing the boundary were appropriately taken into account by monitoring Δr_n displacements for each particle (Kehr and Binder 1983).

At high temperature ($k_B T/J = 0.13$) the self-diffusion coefficients are large and isotropic as is expected: $D_x \simeq D_y \simeq D_z = 0.125(8)$ (figure 3(a)). In the intermediate phase (figure 3(b)) not only is the value of D_n definitely lower but the diffusion becomes anisotropic (at $k_B T/J = 0.11$, $D_z = 0.060(3)$, $D_x \simeq D_y = 0.024(1)$). This anisotropy is characteristic also for the low-temperature phase (figure 3(c)) where, at $k_B T/J = 0.08$, $D_z = 0.0051(5)$; $D_x \simeq D_y = 0.00086(8)$.

Anisotropic diffusion was also observed in the ordered phases of the interacting lattice gases on the square (Sadiq and Binder 1983) and on the FCC (Kutner *et al* 1983) lattices. In these cases the close-packed rows or planes hinder the motion in some directions. In our case the occupied sites in the ordered phase form a BCC structure and the anisotropy is strongly related to the existence of an intermediate phase. In the intermediate phase, two sublattices (e.g. 1 and 4) are equally occupied and the jumps from and to these sublattices are preferred to other ones. Since the 'shortest paths' connecting the sites of sublattices 1 and 4 lie along vertical chains, the motion is more probable in this direction ($D_z > D_x = D_y$). This mechanism also works in the low-temperature ordered phase although sublattices 1 and 4 are not equally occupied. The motion on the vertical chains becomes more dominant at low temperature: the strong first-neighbour repulsion hinders the diffusion in the x, y directions since sublattice 1 is almost fully occupied.

Both in the ordered and in the intermediate phases the anisotropic diffusion can therefore be traced back to the distribution of particles on sublattices which are anisotropically positioned relative to the cage lattice. Anisotropic charge distribution was used to explain the anomalous anisotropic polarisability below 700 K (Mazzacurati *et al* 1982) discovered by Mariotto *et al* (1981). This supports the suggestion of I that the anomalies found in α-AgI may be explained by the intermediate phase of the above lattice gas model. Since the anisotropic diffusion in the partially ordered phase refers to anisotropic conductivity, we are of the view that anisotropic transport properties should be observable in the super-ionic phase of α-AgI for $T < 700$ K.

In the Letter we have demonstrated, using the Monte Carlo method, that in the interacting lattice gas on the non-Bravais lattice formed by the tetrahedral interstitial sites of the BCC lattice an intermediate phase exists and the self-diffusion is anisotropic there. We intend to study this system in more detail and to include collective diffusion, density correlations, and the dependence of these on the parameters.

References

Binder K and Stauffer D 1983 *Applications of Monte Carlo Methods in Statistical Physics, Topics in Current Physics* vol **36**, ed. K Binder (Berlin: Springer) p 1

Horner H and Wagner H 1974 *J. Phys. C: Solid State Phys.* **7** 3305
Kehr K W and Binder K 1983 *Applications of Monte Carlo Methods in Statistical Physics, Topics in Current Physics* vol **36**, ed. K Binder (Berlin: Springer) p 181
Kutner R, Binder K and Kehr K W 1983 *Phys. Rev.* B **28** 1846
Mariotto G, Fontana A, Cazzanelli E, Rocca F, Fontana M P, Mazzacurati V and Signorelli G 1981 *Phys. Rev.* B **23** 4782
Mazzacurati V, Ruocco G, Signorelli G, Cazzanelli E, Fontana A and Mariotto G 1982 *Phys. Rev.* B **26** 2216
Perrott C M and Fletcher N H 1969 *J. Chem. Phys.* **50** 2770
Sadiq A and Binder K 1983 *Surf. Sci.* **128** 350
Shirley A I, Hall C K, Sahni P S and King N J 1984 *J. Chem. Phys.* **81** 4053
Szabó G 1986 *J. Phys. C: Solid State Phys.* **19** to appear