PHASE DIAGRAM OF ADSORBATE-INDUCED ROW-TYPE-ALIGNMENTS

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The phase diagram of adsorbate-induced row-type-alignments, such as missing-row reconstructions induced by adsorbate-atoms on the FCC(110) surface, is calculated by the Blume-Emmery-Griffiths (BEG) model. In the model, we introduce adatom-adatom and dipole-dipole interactions between nearest-neighbor (NN) and next-nearest-neighbor (NNN) rows. The calculation of the temperature versus adatom chemical potential phase diagram is performed using mean-field approximation. It is indicated that when NN and NNN interactions are competitive, there appear either dipole or coverage modulated (incommensurate) phases at high temperatures for wide regime of the interactions.

I. INTRODUCTION

It is well known that row-type-alignments are induced in many cases on transition metal surfaces by adsorbates. A typical example is the (1 × n) missing-row reconstruction (MRR) of FCC(110) metal surface covered by adatoms such as H/Cu(110), O/Rh(110), and O/Pd(110). In these systems, the rows of the metal atoms in [110] directions are accompanied by zigzag chains of adatoms sitting in the threefold FCC hollow sites on the [111] microfacets of the surface and each nth row is missing. It should be noted the arrangement of the missing row at low coverage c of adatoms suggests that the interactions between the rows of the metal atoms are of repulsive.

On the theoretical side, P. J. Kundrotas et al. recently showed that the 2-dimensional Blume-Emmery-Griffiths (BEG)-like model is a useful model to analyze these ordering phenomena of row-type-alignments including the adatom-metal dipoles. Their excellent calculation of the finite temperature phase diagram for O/Rh(110) is, however, restricted to the case where the nearest-neighbor (NN) interactions along [001] direction is much stronger than the next-nearest-neighbor (NNN) interactions.

The purpose of this paper is to extend the analysis, including the ground state analysis, to the case of the relatively strong NNN interactions. In the case of axial-next-nearest-neighbor-Ising (ANNNI) model, when NN and NNN interactions are competitive, an introduction of the relatively strong NNN interactions usually give rise to change of the ground state structures and also induces entropic modulated phases at high temperatures. From this fact, we may expect that the BEG model will also exhibit a rich variety of phases due to the frustration of the interactions.

In this paper, after establishing our model, we determine the ground state phase diagram by energy comparison method. This ground state analysis shows the new structure corresponding to the \(\langle uudd \rangle\) structure of the ANNNI model appears under the certain conditions for NNN interactions. We then derive the mean-field equations to investigate qualitative feature of the finite temperature phase diagrams. Solving the linearized mean-field equations analytically, we obtain the condition for the interactions to realize the stable modulated phases. Numerical analysis of the mean-field equations is performed to calculate the finite temperature phase diagrams for several interaction regimes, including the region satisfying the modulated phase conditions. These analyses show that there appear either dipole or coverage modulated phases at high temperatures for certain regime of the interactions.

Organization of this paper is as follows: In the next section (section II), after setting up the model for the MRR ordering, we construct the ground state phase diagram. Section III deals with derivation of the mean-field equations and solution corresponding to the modulated phase. Section IV is devoted to the numerical analysis. Finally, summary and concluding remarks are given in section V.

II. MODEL AND GROUND STATE ANALYSIS

It is plausible to expect that the clusterlike bonding between metal atom and adatom produces a dipole moment by transfer of electron. In case of zigzag adsorption, there exists the asymmetric bonding between metal atom and adatom. The asymmetry can be theoretically treated by the dipole moments with opposite directions, say "up" or "down" dipoles. Therefore, a site of the surface where metal atom sits in is in one of three states, missing of metal atom (vacant), occupied by metal atom with "up" or "down" dipoles.

In order to analyze the ordering phenomena of row-type-alignments including the adatom-metal dipoles, we introduce pseudo "spin" variable \(\sigma_i\) at i site to represent
the three states of the site $i$, vacant ($\sigma_i = 0$), occupied by metal atom with "up" or "down" dipoles ($\sigma_i = \pm 1$).

Since the occupation number of metal atom (accompanied by adatom) at $i$ site is given by $\sigma_i^2$, the Hamiltonian of the system is represented by the BEG model as

$$
\mathcal{H} = \sum_{ij} J_{ij} \sigma_i \sigma_j + \sum_{ij} K_{ij} (\sigma_i^2 - 2/3)(\sigma_j^2 - 2/3)
+ \mu \sum_{i} (\sigma_i^2 - 2/3)
$$

(1)

where $J_{ij}$ ($K_{ij}$) is interaction between $ij$ pair of the dipoles (metal atoms), $\mu$ is the chemical potential. $\sigma_i^2 = 1(0)$ means a metal atom occupies the surface site $i$ (or not). Here we use $(\sigma_i^2 - 2/3)$ instead of $\sigma_i^2$ for convenience of the later calculation. Following P. J. Kundrotas et al., we assume that

$$(J_{ij}, K_{ij}) = \begin{cases} 
(J_0, K_0) & ij = \text{NN pair in [110] direction} \\
(J_1, K_1) & ij = \text{NN pair in [001] direction} \\
(J_2, K_2) & ij = \text{NNN pair in [001] direction} \\
(0, 0) & \text{otherwise}
\end{cases}
$$

(2)

and farther neighbor interactions are negligible. Then the Hamiltonian is rewritten as

$$
\mathcal{H} = \sum_{\ell, m} \left\{ J_0 \sigma_{\ell m} \sigma_{\ell m+1} + K_0 (\sigma_{\ell m}^2 - 2/3)(\sigma_{\ell m+1}^2 - 2/3) \\
+ J_1 \sigma_{\ell m} \sigma_{\ell m+1} + K_1 (\sigma_{\ell m}^2 - 2/3)(\sigma_{\ell m+1}^2 - 2/3) \\
+ J_2 \sigma_{\ell m} \sigma_{\ell m+2} + K_2 (\sigma_{\ell m}^2 - 2/3)(\sigma_{\ell m+2}^2 - 2/3) \\
+ \mu (\sigma_{\ell m}^2 - 2/3) \right\}
$$

(3)

where $\ell$ ($m$) refers site-number along [001] ( [110]), namely $\ell$ ($m$)-direction.

In the MRR-type-alignments, metal atoms form a chain-like structure and the adatoms are ordered in zigzag arrangement which corresponds to "antiferromagnetic" ordering of the $\sigma_{\ell m}$ along $m$-direction. From these experimental facts, the interactions in Eq.(3) should satisfy the

$$
J_0 > 0 \ , \ K_0 < 0 \ , \ K_1 > 0 \ , \ K_2 > 0 
$$

(4)

It should be noted that the Hamiltonian (3) can be transformed into "ferromagnetic" ($J_0 < 0$) one by the transformation $\sigma_{\ell m} \rightarrow (-1)^m \sigma_{\ell m}$.

Now we determine the ground state phase diagram by comparing the energies of several "spin" arrangements. From the condition $J_0 > 0$ and $K_0 < 0$, the "spin" arrangement in the ground state is expected to be represented by $m$-independent "spin" $\sigma_{\ell}$ as

$$
\sigma_{\ell m} = (-1)^m \sigma_{\ell}
$$

(5)

To represent the "spin" arrangement, we introduce the notation which indicates the repeating unit of $\sigma_{\ell}$ as $\langle \sigma_1 \sigma_2 \cdots \sigma_n \rangle$; for example $\langle ud0 \rangle$ represents the "spin"

![Figure 1](attachment:image.png)

FIG. 1. Ground state phase diagrams for $K_0 < 0$, $J_0 > 0$ and $K_i > |J_i| (i = 1, 2)$ in $k_2$-$\mu_2$ plane, where $k_2 = (K_2 - |J_2|)/(K_1 - |J_1|)$ and $\mu_2 = (-\mu + \sqrt{(K_0 + K_1 + K_2) + |J_0| - K_0})/(K_1 - |J_1|)$; (a:upper) for $J_1 > 0$, $J_2 > 0$; (b:lower) for $J_1 < 0$, $J_2 < 0$. Boundary lines in the diagrams are described as: $\mu_2 = 0$ for $\langle u00 \rangle$; $\mu_2 = 3k_2$ for $\langle uu00 \rangle$ and $\langle ud0 \rangle$ in (a), for $\langle u00 \rangle$ and $\langle u \rangle$ in (b); $\mu_2 = 3/2$ for $\langle uu0 \rangle$ and $\langle uu00 \rangle$ in (a), for $\langle uu0 \rangle$ and $\langle ud0 \rangle$ in (b); $\mu_2 = 2 - k_2$ for $\langle ud0 \rangle$ and $\langle ud00 \rangle$ in (a), for $\langle ud0 \rangle$ and $\langle uu0 \rangle$ in (b); $k_2 = \mu_2/2 - 1/4$ for $\langle uu00 \rangle$ and $\langle ud0 \rangle$ in (a), for $\langle uu00 \rangle$ and $\langle uu0 \rangle$ in (b); $k_2 = (\mu_2 - \Delta_J)/2$ for $\langle ud0 \rangle$ and $\langle ud0 \rangle$ in (a) where $\Delta_J = Min\left\{6J_2/(K_1 - |J_1|), 3J_1/(K_1 - |J_1|)\right\}$; $k_2 = (\mu_2 - 2)/2$ for $\langle u00 \rangle$ and $\langle u \rangle$ in (b).

arrangement with repeating unit $\langle \hat{\sigma}_1 \hat{\sigma}_2 \hat{\sigma}_3 \rangle = (\pm 1 \ - 1 \ 0)$. The target "spin" arrangements of the energy comparison are

Case A: $J_1 > 0 \ , \ J_2 > 0$
the occupation number of metal atom (accompanied by atomic concentration of metal or adatom (coverage) at state $J$),

Case B: $J_1 < 0$, $J_2 < 0$

It is noticed that the results for the case C: $J_1 < 0$, $J_2 > 0$ (case D : $J_1 > 0$, $J_2 < 0$ ) can be easily obtained from the results for case A (case B) by the transformation $\delta_\ell \rightarrow (-1)^\ell \delta_\ell$.

Figure 1 shows the ground state phase diagram in $\mu_2$, $k_2$ plane obtained under the condition $K_i > |J_i| (i = 1, 2)$, where $\mu_2$ and $k_2$ are given as

$$ k_2 = \frac{(K_2 - |J_2|)}{(K_1 - |J_1|)} , \quad \mu_2 = \frac{-\mu + \frac{8}{9}(K_0 + K_1 + K_2)}{|J_0| - K_0)}/(K_1 - |J_1|) . $$

For large $\mu_2$ regime in Fig.1(a), either $\langle ud \rangle$ or $\langle uudd \rangle$ is realized depending upon $2J_2 < J_1$ or $2J_2 > J_1$, respectively.

For large $K_2$, the energetically preferable structure may be the one containing no $K_2$ bonding, such as $\langle u00 \rangle$ or $\langle u0d0 \rangle$. Actually, as is shown in Fig. 1, there appears either $\langle uuu0 \rangle$ or $\langle u0d0 \rangle$ depending size of $J_1$ for the relatively large $K_2$. Therefore we might observe the different sequences of the MRR with increasing the chemical potential if we prepare the surface with relatively large $K_2$. It is remarked here that there exist many structures degenerate in energy in the region of the phase containing two adjacent "0". For example, structures consisting of any combination of $\langle u0 \rangle$ ($\langle u0d0 \rangle$ and $\langle d0 \rangle$) ($\langle d0u0 \rangle$) are degenerate in energy with the structure $\langle u0 \rangle$ ($\langle u0d0 \rangle$).

### III. MEAN-FIELD ANALYSIS AND MODULATED PHASES

In this section we derive the mean-field equations to construct phase diagrams at finite temperatures. The mean-field energy $\epsilon$ per $m$-direction line is obtained as

$$ \epsilon = \sum_{\ell} \left\{ |J_0| x_\ell^2 + \frac{K_0}{9} (y_\ell^2 + 2) + J_1 x_\ell x_{\ell+1} + \frac{K_1}{9} (y_\ell y_{\ell+1} + 2) + J_2 x_\ell x_{\ell+2} + \frac{K_2}{9} (y_\ell y_{\ell+2} + 2) - \frac{\mu}{3} y_\ell \right\} . \tag{8} $$

where $x_\ell$ and $y_\ell$ are $m$-independent thermal average of $(-1)^m \sigma_\ell^m$ and $(2 - 3\sigma_\ell^2)$, respectively. Since $\sigma_\ell^m$ is the occupation number of metal atom (accompanied by adatom) at $\ell m$ site, as mentioned in previous section, $c_{\ell} = (2 - y_\ell)/3$ gives the $m$ independent thermal average of atomic concentration of metal or adatom (coverage) at $\ell m$ site.

The mean-field entropy $s$ per $m$-direction line can be expressed in a unit of $k_B = 1$ by $x_\ell$ and $y_\ell$ as

$$ s = -\sum_{\ell} \sum_\sigma R_\ell(\sigma) \{ \log R_\ell(\sigma) - 1 \} . \tag{9} $$

where $R_\ell(\sigma)$ is the $m$ independent probability of finding the $\ell m$ site at state $\sigma$ given as

$$ R_\ell(\sigma) = \frac{1}{3} (1 + 3\sigma x_\ell/2 + (2 - 3\sigma^2) y_\ell/2) . \tag{10} $$

Optimization of the free energy $f = \epsilon - Ts$ per line with respect to $x_\ell$ and $y_\ell$ leads the so called mean-field equations as

$$ -2|J_0|x_\ell + J_1(x_{\ell-1} + x_{\ell+1}) + J_2(x_{\ell-2} + x_{\ell+2}) + T\sum_{\sigma} \frac{\sigma}{2} \log R_\ell(\sigma) = 0 , \tag{11} $$

$$ \frac{2K_0}{9} y_\ell + \frac{K_1}{9} (y_{\ell-1} + y_{\ell+1}) + \frac{K_2}{9} (y_{\ell-2} + y_{\ell+2} + 2) - \frac{\mu}{3} + T\sum_{\sigma} \frac{(2 - 3\sigma^2)}{6} \log R_\ell(\sigma) = 0 . \tag{12} $$

where $T$ is the temperature.

When $\mu = 0$, we easily obtain a stable "paramagnetic" solution $x_\ell = 0$ and $y_\ell = 0$ with coverage $c = 2/3$ at high temperatures. To determine the transition temperature from the "paramagnetic" phase and the phase just below the transition temperature, we linearize the mean-field equations. Substitution of $x_\ell = X_\ell \exp(iq\ell)$ and $y_\ell = Y_\ell \exp(iq\ell)$ in the linearize equations leads us to the transition temperature at $\mu = 0$ as maximum of

$$ T_x(q) = \frac{4}{3} (|J_0| - J_1 \cos(q) - J_2 \cos(2q)) , \tag{13} $$

$$ T_y(q) = \frac{4}{9} (-K_0 - K_1 \cos(q) - K_2 \cos(2q)) . \tag{14} $$

When NNN interactions $|J_2|$, $|K_2|$ are very small, either $q = 0$ or $q = \pi$ gives the maximum and there appears no modulated phases. On the other hand, if NNN interactions satisfy the condition

$$ |J_2/J_1| > 1/4 (J_2 > 0) \quad \text{or} \quad |K_2/K_1| > 1/4 (K_2 > 0) \tag{15} $$

the system just below the transition temperature exhibits the modulated phase characterize by wave number $\cos(Q) = -J_1/4J_2$ (dipole modulation) or $\cos(Q) = -K_1/4K_2$ (coverage modulation).

### IV. NUMERICAL RESULTS

Since it is difficult to solve the mean-field equations analytically, we have to solve the equations numerically to obtain the phase diagrams. In the present paper, we confine ourselves to the case of "ferromagnetic" interactions between rows, i.e. $J_1 < 0$ and $J_2 < 0$. To demonstrate the change of ground state and appearance of the modulated phase, we deal with the three cases of interaction regime,

a) $J_0 = 1$, $K_0 = -3$, $J_1 = -1$, $K_1 = 3$, $J_2 = -0.05$, and $K_2 = 0.5$,
b) $J_0 = 1, K_0 = -3, J_1 = -1, K_1 = 3, J_2 = -0.05$, and $K_2 = 1.55$.

c) $J_0 = 1, K_0 = -3, J_1 = -0.5, K_1 = 3, J_2 = -0.03$, and $K_2 = 0.88$.

The interaction constants in the case a) are the same as Ref. [5] those in the case b) correspond to the regime $k_2 = 0.75 (> .5)$ where the $\langle uu00 \rangle$ appears as ground state (see Fig.1(b)); those in the case c) satisfy the condition $K_2/K_1 (= 0.29333) > 1/4(K_2 > 0)$; the modulated phase is expected to exist.

To construct the phase diagrams for the three cases of interaction regime at finite temperatures, we solve the mean-field equations within repeating unit 12, i.e.

$(x_{12+\ell}, y_{12+\ell}) = (x_\ell, y_\ell)$ $(\ell = 1, 2, \cdots, 12)$, for various values of temperatures and chemical potential $\mu_2$ in Fig.1(b) along the line $k_2 = 0.225$ (case a), the line $k_2 = 0.75$ (case b)) and the line $k_2 = 0.34$ (case c)).

The calculated $T$ versus $\mu$ phase diagrams for the cases a), b), and c) are shown in Fig. 2(a), (b), and (c), respectively. In the figures, $u/d$ denotes the "paramagnetic" row with $x = 0$ and $y \neq 0$.

It is natural to expect that at low temperatures, there appear successively the phases corresponding to the ground state structures with increasing chemical potential; at high temperatures the rows prefer the "paramagnetic" state to "magnetic" state to gain free energy by entropy term. As seen in Figs.2(a) to (c), all of our phase diagrams show this tendency.

It is clear that the phase diagram in Fig. 2(a) is the topologically same as that in Ref. [5]. This confirms qualitative feature of our calculation. Major differences between our results and those of Ref. [5] are the transition temperature of our mean-field calculation being as much as twice of that in Ref. [5] and existence of the "magnetic" phase $\langle uu00 \rangle$ phase at low temperatures.

As shown in Fig. 2(b), $\langle uu00 \rangle$ phase corresponding to the ground state structure in which two out of four rows of metal atoms are missing appears for a certain range of chemical potential at low temperatures. P. J. Kundra et al. did not take this $\langle uu00 \rangle$ into account. From predictions, the modulated phase accompanied by the wave number $Q = \cos^{-1} (-K_1/4K_2)$ should appear in this case. However, we could not find it because our calculation is limited within the periodicity 12 and not
enough big to find it.

Fig. 2(c) shows the phase diagram for the case c) where the condition $K_2/K_1 > 1/4$ ($K_2 > 0$) is satisfied. Therefore, the modulated phase with the wave number $Q = \cos^{-1}(-K_1/4K_2) \simeq Q_1 = 10\pi/12$ should appear in this case. Actually, we obtain within repeating unit 12 the stable modulated phase shown in Fig. 3 in the vicinity of the point $(\mu = 0, T_y(Q_1))$. In the figure, $r$ represents the row numbers along the [001] direction on the FCC(110) surface and $y_r = 2 - 3c_r$, where $c_r$ describes the probability that a metal atom row exists at the $r$th row. In comparison with the structure $\langle uu0 \rangle$ at lower temperatures in the case (shown in Fig. 2(c)), the distribution of metal atom rows along the [001] direction on the FCC(110) metal surface is modulated. Thus our numerical results are consistent with the predictions. Although it will be difficult to find out experimentally the modulated phase, we show a possibility of realization of the modulated phases.

The details of the present calculation will be published near future.

FIG. 3. $r$-dependence of $y_r$ in the modulated phase. The dotted line represents $0.6 \cos(Q_1(r - 6)) - 0.1 \cos(Q_2(r - 6))$, where $Q_1 = 10\pi/12$, and $Q_2 = 9\pi/12$.

V. SUMMARY

The ground state and finite temperature phase diagrams of adsorbate-induced row-type-alignments is calculated by the Blume-Emmery-Griffiths (BEG) model. In the model, we introduce adatom-adatom and dipole-dipole interactions between nearest-neighbor (NN) and next-nearest-neighbor (NNN) rows.

The ground state analysis shows the new structure corresponding to the $\langle uu0d \rangle$ structure of the ANNNI model appears under the certain conditions for NNN interactions.

For the finite temperature, we obtain the condition for the interactions to realize the stable modulated phases by solving the linearized mean-field equations analytically.

Numerical analysis of the mean-field equations is performed to calculate the finite temperature phase diagrams for several interaction regimes, including the region satisfying the modulated phase conditions. These analyses show that there appear coverage modulated (incommensurate) phases at high temperatures for certain regime of the interactions.

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