Short-range correlations in binary alloys: Spin model approach to Ag_{0.5}Pd_{0.5}

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Short-range correlations in Ag-Pd alloys are investigated by analyzing the \textit{ab initio} total energy of fcc based random Ag_{0.5}Pd_{0.5}. Since the information on the atomic interactions is incorporated in the energetics of alloys it is possible with a suitable model, Bethe-Peierls-Weiss model is used in the present work, to invert the problem, i.e. to obtain information on the short-range correlation from the total energy of a random system. As an example we demonstrate how site correlations can be extracted from random alloy data. Bethe-Peierls-Weiss model predicts positive first neighbor correlator and mixing energy for substitutional face centered cubic (fcc) Ag-Pd alloys at low temperature which can be related to the optimal structures of Ag_{0.5}Pd_{0.5}.

I. INTRODUCTION

The low-temperature short-range order of Ag-Pd has attracted theoretical research for several decades. Results supporting phase separation have been reported. Due to the low transition temperature predicted for the disorder-order transition there are no direct experimental observation concerning this matter.

In the present work, we reanalyze the Ag-Pd binary alloy system using a spin lattice model beyond the simplest mean field (Weiss) model. We employ Bethe-Peierls-Weiss (BPW) model\cite{BPW}, which, in contrast to Weiss model, incorporates non-vanishing correlators of neighbor sites. Therefore it is suitable for extracting ordering information on the binary system in hand.

II. BPW MODEL

The lattice structure of binary alloys can be modeled by spin (Ising) lattices identifying spin states \pm 1 of a particular site with occupation of a given atom, say A or B. For spin model calculations one has to specify the interaction energies between the sites. This can be done, for instance, by fitting the calculated lattice quantities to the corresponding observed or simulated ones.

In the following we model Ag-Pd by an Ising-lattice with \( N \) sites each associated with spin \( \sigma_i = \pm 1, i = 1, \ldots N \). We identify the spin state \( \sigma_i = +1 \) with the occupation of the site \( i \) by a Ag atom and \( \sigma_i = -1 \) with the occupation of the site \( i \) by a Pd atom. The average concentration of the whole lattice is fixed by requiring that there is \( N_+ \) sites with \( \sigma_i = +1 \) and \( N_- \) sites with \( \sigma_i = -1 \) \((N_+ + N_- = N)\). The average concentration of Ag atoms is then \( c = N_+/N \) and the expectation value over all lattice sites is

\[
\langle \sigma \rangle = \frac{\sum_i \sigma_i}{N} = \frac{N_+ - N_-}{N} = 2c - 1. \tag{1}
\]

Considering only two-particle interactions the state sum is

\[
Z = \sum_{\{\sigma_i\}_{i=1}^N} e^{-\beta E}, \tag{2}
\]

where the sum is over all spin configurations with constraint \( \sum_i \sigma_i = (2c - 1)N \). The total energy \( (E) \) is written as the sum of pairwise interaction energies

\[
E = \frac{1}{2} \sum_{i \neq j} E_{ij} = \sum_{i > j} E_{ij}. \tag{3}
\]

An important quantity measuring the ordering of spins is the correlator

\[
g_{i,j} = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle. \tag{4}
\]

Here \( g_{i,j} \in [-1, 1], g_{i,j} < 0 (> 0) \) corresponds to spins at sites \( i \) and \( j \) tending to align antiparallel (parallel), whereas the case \( g_{i,j} = 0 \) corresponds to completely random alignment.

In practise to calculate the state sum in Eq. (2) one has to make further approximation. In the following we use the nearest neighbor (NN) approximation, where only the closest atom sites are included in the energy sum \([3]\). While Ising models include only two-site interactions, our task requires to include the multi-site interactions to the model. Formally this is done by allowing the Ising model parameters to depend on the concentration \( c \), so that many-site interactions are effectively and on the average taken into account.

Thus in NN-models only the nearest neighbor sites contribute to the energy and for a fixed concentration \( c \) only effective energy for a site is given. For that purpose we define the pair interaction energy as

\[
E_{ij} = \begin{cases} 
\epsilon(c) + \Delta\epsilon(c) \sigma_i \sigma_j + \frac{1}{2} \tilde{\epsilon}(c) (\sigma_i + \sigma_j) & \text{if } i,j \text{ are NN} \\
0 & \text{otherwise}
\end{cases} \tag{5}
\]

Suppose now, that the site \( i \) of the Ising-lattice has \( \nu_i \) nearest neighbors \( j \in N_i \). This number \( \nu_i \) is the coordination number of the site \( i \). Then the energy of the whole system is

\[
E = \frac{1}{2} \sum_{i \neq j} E_{ij} = \frac{1}{2} \sum_{i=1}^N \sum_{j \in N_i} E_{ij} = \frac{1}{2} \sum_{i=1}^N E_i, \tag{6}
\]
where
\[ E_i = \sum_{j \in N_i} E_{ij} \]  
(7)
is the effective energy of the site \( i \). In this sum there is \( n_i \) addends and reads for \( i \)

\[ E_i = n_i (\epsilon + \frac{1}{2} \bar{\epsilon} \sigma_i + (\Delta \epsilon \sigma_i + \frac{1}{2} \bar{\epsilon}))(\sum_{j \in N_i} \sigma_j) \]  
(8)

To go beyond mean field models we treat the system by BPW model\[12]\. In BPW model each site \( i \) interacts with its \( \nu \) nearest neighbors \( i_1, \ldots, i_\nu \), which in part interact with their NN’s other that \( i \) itself, i.e. with \( \nu - 1 \) sites. The interaction energy of neighbors of \( i \) is included exactly, whereas the interaction of the neighbors with their neighbors is calculated using mean field. Thus, instead of Eq. (7) the energy of a site \( i \) is

\[ E_i = \sum_{j \in N_i} E_{ij} + k \sum_{j \in N_i, l \in N_i, \ j \neq l} (E_{jl})_{\sigma_i} \]

\[ \quad = \nu \epsilon + \frac{1}{2} \nu \bar{\epsilon} \sigma_i + (\Delta \epsilon \sigma_i + \frac{1}{2} \bar{\epsilon})(\sigma_{i_1} + \cdots + \sigma_{i_\nu}) \]

\[ + k(\nu - 1)[\nu \epsilon + (\Delta \epsilon \sigma_i + \frac{1}{2} \bar{\epsilon})(\sigma_{i_1} + \cdots + \sigma_{i_\nu}) \]

\[ + \frac{1}{2} \nu \bar{\epsilon} \langle \sigma \rangle], \]

where \( k \) is a combinatorial parameter used to obtain specific thermodynamic quantities by differentiation and the choice \( k = 1 \) corresponds to the normal BPW model. For Ag-Pd the pair interactions just at the first two coordination shells are needed to qualitatively understand the ordering energy.

For \( \nu \) NNs of site \( i \) we denote the number of \( \sigma_{ij} = +1 \) by \( n_+ \) and the number of \( \sigma_{ij} = -1 \) by \( n_- \), so that \( n_+ + n_- = \nu \) and

\[ E_i = E(\sigma_i, n_+) \equiv \nu \epsilon + \frac{1}{2} \epsilon \nu \sigma_i + (\Delta \epsilon \sigma_i + \frac{1}{2} \bar{\epsilon})(n_+ - n_-) \]

\[ + k(\nu - 1)[\nu \epsilon + (\Delta \epsilon \sigma_i + \frac{1}{2} \bar{\epsilon})(n_+ - n_-) + \frac{1}{2} \nu \bar{\epsilon} \langle \sigma \rangle] \]

\[ = \nu \left[ \epsilon - \frac{1}{2} \epsilon + k(\nu - 1) \left\{ \epsilon - \Delta \epsilon \langle \sigma \rangle - \frac{1}{2} \epsilon (1 - \langle \sigma \rangle) \right\} \right] \]

\[ + \nu \frac{1}{2} \bar{\epsilon} - \Delta \epsilon \sigma_i \]

\[ + \left[ \Delta \epsilon \sigma_i + \frac{1}{2} \epsilon + k(\nu - 1) \left\{ \Delta \epsilon \langle \sigma \rangle + \frac{1}{2} \epsilon \right\} \right] n_+, \]

(10)

When \( n_+ \ll N_+ \) and \( \nu \ll N \) we may approximate that configuration of the \( \nu \) neighbors of a fixed site \( i \) is effectively independent on all other sites. This is the main idea of Bethe-Peierls approximation\[13]\. However, BPW-approximation is widely used to model short-range correlation in various statistical systems\[13,14\]. The validity of this approximation is however not clear, as there is no known error estimation method; PBW model has an uncontrolled error. Anyway, with this assumption of effective independence of neighbors of separate sites leads to partition function

\[ Z = \prod_{\{\sigma_i\}_{i=1}^N} e^{-\frac{1}{\beta} E_i} = \left( \frac{N}{N_+} \right)^{N_+} \left( \frac{N}{N_-} \right)^{N_-}, \]  
(11)

where \( \beta = (k_B T)^{-1} \), \( k_B \) is the Boltzmann constant and \( T \) temperature.

The effective one site (neighbor) partition function for spin \( \sigma \) can be calculated using grand canonical ensemble of its neighbors. We write

\[ Z_1(\sigma) = \sum_{n_+ = 0}^{\nu} \left( \frac{\nu}{n_+} \right) e^{\mu n_+} e^{-\frac{1}{\beta} E(n_+ \sigma)}. \]  
(12)

The chemical potential of a site \( \mu \) has to be related to the overall concentration \( c \), as \( N_+ \) is still fixed by overall concentration condition \( c = N_+ / N \).

Here the partition function \( Z \) is a grand canonical partition function with respect to the number of \( \sigma = +1 \) sites of the system but canonical one with respect to the total number of sites. That is, the partition function is related to grand potential

\[ \Omega = -\frac{1}{\beta} \ln Z. \]

Thus when we later turn to use Helmholtz free energy (i.e fixed concentration) we have to make the appropriate Legendre transformation.

The thermodynamical quantities are to be calculated from the logarithm of the partition function, i.e.

\[ \ln Z = \ln \left( \frac{N}{N_+} \right) - \frac{1}{2} N \beta [E_0 + c \Delta E(+1) + (1 - c) \Delta E(-1)] \]

\[ + N \left\{ \nu \epsilon \ln \left[ 1 + z e^{-\beta E_1} \right] \right\} + \nu (1 - c) \ln \left[ 1 + z e^{-\beta E_1} \right] \]

(13)

with

\[ E_0 = \nu \left[ \epsilon - \frac{1}{2} \bar{\epsilon} \right] \]

\[ + k(\nu - 1) \left\{ \epsilon - \Delta \epsilon \langle \sigma \rangle - \frac{1}{2} \epsilon (1 - \langle \sigma \rangle) \right\} \]

\[ = \nu \left[ \nu \epsilon - \nu \bar{\epsilon} \right] + \frac{1}{2} \nu \bar{\epsilon} - \Delta \epsilon \sigma_i \]

\[ + \left[ \Delta \epsilon \sigma_i + \frac{1}{2} \epsilon + k(\nu - 1) \left\{ \Delta \epsilon \langle \sigma \rangle + \frac{1}{2} \epsilon \right\} \right] n_+. \]

\[ \Delta E(\sigma) = \Delta E = \nu \left[ \frac{1}{2} \bar{\epsilon} - \Delta \epsilon \sigma \right], \]

\[ \bar{E}(\sigma) = \Delta \epsilon \sigma + \frac{1}{2} \epsilon + k(\nu - 1) \left\{ \Delta \epsilon \langle \sigma \rangle + \frac{1}{2} \epsilon \right\} \]

\[ = \Delta \epsilon \sigma + \nu \left[ \frac{1}{2} \bar{\epsilon} + k(\nu - 1) \Delta \epsilon \sigma \right] \]
where \( z = e^\mu \) is the one-site fugacity

\[
z^{-1} = \frac{\sqrt{\langle \sigma \rangle^2 + (1 - \langle \sigma \rangle^2) e^{-\beta (\bar{E}_+ - \bar{E}_-)} - \langle \sigma \rangle \cdot 1}}{1 + \langle \sigma \rangle}
= \frac{\sqrt{\langle \sigma \rangle^2 + (1 - \langle \sigma \rangle^2) e^{-2 \bar{E} \Delta \epsilon - \langle \sigma \rangle} \cdot e^{-\beta \bar{E}_-}}}{1 + \langle \sigma \rangle},
\]

(14)

Thus BPW model clearly allows correlation between a site and its neighbors.

The mixing energy per atom can be constructed straightforwardly as

\[
uu_{\text{mix}}(c) = u(c) - c u(1) - (1 - c) u(0).
\]

By differentiation of (13) with respect to energy parameters \( \epsilon \) and \( \Delta \epsilon \) we find

\[
g_{i, i+1} = [1 - (\sigma)^2] \left[ \frac{1}{1 + z^{-1} e^{\beta \bar{E}_+}} - \frac{1}{1 + z^{-1} e^{\beta \bar{E}_-}} \right].
\]

(20)

Thus BPW model clearly allows correlation between a site and its neighbors.

### III. RESULTS

Next step is to determine the BPW parameters \( \epsilon \), \( \bar{\epsilon} \) and \( \Delta \epsilon \) by fitting the internal energy to the calculated total energy of Ag,Pd\(_{1-c}\) alloys. The reference data we are using are the total energies from Ref. [15] calculated for Ag,Pd\(_{1-c}\) using the exact muffin-tin orbitals method [16,17] within the coherent potential approximation [18,19], i.e. corresponding to the mean field approximation (Table III)). Because the \textit{ab initio} energies in Table I refer to the non-correlated Ag-Pd system at 0 K temperature we have to use in the fitting procedure the non-correlated BPW energy obtained by differentiation with respect to \( k \) or equivalently from Eq. (10) as

\[
u = \frac{1}{2 N} \sum_{i=1}^{N} (E_i),
\]

assuming that \( \langle \sigma_i \sigma_j \rangle = \langle \sigma_i \rangle \langle \sigma_j \rangle = \langle \sigma \rangle^2 (i \neq j) \). We find the non-correlated internal energy \( u_{nc} \) to be up to normalization same as in the Weiss model,

\[
uu_{nc}(\sigma) = \frac{1}{2} \nuu\nuu(\epsilon + \bar{\epsilon} + \Delta \epsilon \langle \sigma \rangle^2).
\]

(21)

This can be expressed as a function of concentration as

\[
uu_{nc}(c) = \frac{1}{2} \nuu\nuu(\epsilon c + \bar{\epsilon} c + \Delta \epsilon \epsilon c^2),
\]

(22)

where the parameters are related by

\[
\Delta \epsilon = \frac{1}{4} \Delta \epsilon c,
\]

\[
\bar{\epsilon} = \frac{1}{2} (\Delta \epsilon c + \epsilon c),
\]

(23)

\[
\epsilon = \epsilon c + \bar{\epsilon} c + \Delta \epsilon c^2.
\]

| \( c \) | \( u_{nc}(c) [\text{Ry}] \) |
|-------|------------------|
| 0.00  | -10084.720387    |
| 0.05  | -10111.737114    |
| 0.10  | -10138.743066    |
| 0.20  | -10192.765913    |
| 0.40  | -10300.812124    |
| 0.50  | -10354.835440    |
| 0.60  | -10408.858240    |
| 0.70  | -10462.880386    |
| 0.80  | -10516.901915    |
| 0.90  | -10570.922942    |
| 1.00  | -10624.943741    |

Table I: The \textit{ab initio} internal energy of Ag,Pd\(_{1-c}\) at 0 K as obtained in Ref. [12].

To fit the Eq. (22) to the numerical data shown in Table III is not an unambiguous procedure. Several justified
strategies can be introduced to define the concentration dependence of the parameters $\epsilon_e$, $\epsilon_c$, and $\Delta \epsilon_e$. We study four different fitting schemes and compare their results with the data obtained from impurity calculations for Ag-Pd system. In three first fitting schemes we take $\epsilon_c$ and $\epsilon_e$ to be constants whereas different boundary conditions for $\Delta \epsilon_e$ are introduced.

i) The choice $\Delta \epsilon_e(1) = \Delta \epsilon_e(0) = 0$ leads to the correct linear form of the total energy in the limit of noninteracting atoms. This leads to tenth degree interpolation polynomial for $\Delta \epsilon_w(c)$.

ii) Since the term $c^2 \Delta \epsilon_e(c)$ vanish at $c = 0$ the above constraint can be lifted to $\Delta \epsilon_e(1) = 0$. This leads to ninth degree interpolation polynomial for $\Delta \epsilon_w(c)$.

iii) Fitting of eight degree polynomial to the data in Table [I] and interpreting the two terms of lowest degree as $\epsilon_e c$ and $\epsilon_c$, now neither $\Delta \epsilon_e(0) = 0$ nor $\Delta \epsilon_w(1) = 0$.

iv) Redlich-Kister (RK) parameterization\textsuperscript{20} for Eq. \textsuperscript{22}

\[ u_{nc}(c) = \frac{1}{2} \nu[c \epsilon_{RK} + \epsilon_{RK} c + c(1-c) \Delta \epsilon_{RK}(c)]. \]  

(24)

Part of the linear term in \textsuperscript{22} is included to the RK-interaction term. Note, that here $\epsilon_{RK}$ and $\epsilon_{RK}$ are constants. Thus $\epsilon_e = \epsilon_{RK}$, $\epsilon_c = \epsilon_{RK} + \Delta \epsilon_{RK}$ and $\Delta \epsilon_w(c) = -\Delta \epsilon_{RK}$. The RK-parameterization is symmetric in the exchange of Pd$\leftrightarrow$Ag.

To decide which one of the above fitting procedures describes best the energy of Ag-Pd alloy we compare the parameters $\epsilon(c)$, $\bar{\epsilon}(c)$, and $\Delta \epsilon(c)$ at both ends ($c = 0$, $c = 1$) with the corresponding calculated data of Ag-Pd. The reference parameters are shown in Table [II]

| $c$ | $\epsilon$ [Ry] | $\bar{\epsilon}$ [Ry] | $\Delta \epsilon$ [$\mu$Ry] |
|-----|-----------------|-----------------|-----------------|
| 0.00 | -143.817139 | -3.75158336 | -5.555558 |
| 0.05 | -143.817143 | -3.75159123 | -9.409742 |
| 0.10 | -143.817147 | -3.75159910 | -13.425927 |
| 0.20 | -143.817154 | -3.75161484 | -21.296297 |
| 0.40 | -143.817159 | -3.75162327 | -25.513510 |
| 0.50 | -143.817159 | -3.75162367 | -25.712963 |
| 0.60 | -143.817153 | -3.75161104 | -19.396219 |
| 0.70 | -143.817144 | -3.75159374 | -10.743555 |
| 0.80 | -143.817135 | -3.75157664 | -2.199074 |
| 0.90 | -143.817128 | -3.75156189 | 5.178326 |
| 1.00 | -143.817123 | -3.75155107 | 10.587963 |

TABLE III: Energy parameters $\epsilon$, $\bar{\epsilon}$, and $\Delta \epsilon$ as a function of concentration according to the fitting scheme (iii).

It turns out that the fitting procedure (iii) gives the best overall agreement with the \textit{ab initio} impurity data. The BPW parameters obtained from the fit (iii) are shown in Table [III]. Using the BPW parameters various thermodynamic and statistical quantities can be calculated for Ag$_x$Pd$_{1-x}$. Figures [I] and [2] show the mixing energy and the neighbor correlator at different temperatures.

At low temperatures the mixing energy and the neighbor correlator are positive suggesting that the BPW multisite interactions drive substitutional fcc Ag-Pd to favor an atom and its neighbors to be of the same type. This suggests phase separation or segregation tendency for Ag-Pd alloys within substitutional fcc structures at low temperatures in agreement with the results of Refs. [I] and [2]. However, as the recent investigations of Delczeg-Cirjak et al.\textsuperscript{22} show the ground state structure of Ag$_{50.5}$Pd$_{49.5}$ is not a substitutional fcc type structure but the L$_{11}$ type structure with $c/a$ larger than its ideal value. Here $c$ and $a$ are the lattice parameters in hexagonal representation. In conventional cubic coordinate system $c$ axis is along the [111] direction and the lattice parameter $a$ is in the (111) plane. For ideal fcc structure $c/a = \sqrt{6}$, whereas $c$ is the diagonal of the conventional cube and $a$ is the nearest neighbor distance. Since the L$_{11}$ structure is composed of alternating Ag and Pd (111) layers the increasing of $c/a$ compared to the ideal value means, that the nearest neighbor distance of unlike pairs becomes larger than that of like pairs. This shifts more weight on the like-pair interaction than on the mixed-pair interaction. Therefore, the results of BPW model are consistent with the predicted tendency of Ag$_{50.5}$Pd$_{49.5}$ at lower temperatures to order in L$_{11}$ structure with increased $c/a$.

At medium temperatures (50 – 100 K) the mixing energy is negative but the maximum at about $c = 0.5$ suggests a slight tendency of phase separation. At high temperatures the BPW mixing energy approaches the experimental mixing enthalpy\textsuperscript{24} which has its minimum at about $c = 0.6$.

IV. SUMMARY

We have used the Bethe-Peierls-Weiss model to investigate the effect of multisite interactions on the ordering in Ag-Pd alloys. The mean field \textit{ab initio} data has been used to determine the parameters of the BPW model. The BPW mixing energy and neighbor correlator for a substitutional fcc structure of Ag-Pd are positive at low temperatures supporting the stability of the L$_{11}$ struc-
ture of Ag$_{0.5}$Pd$_{0.5}$ with elongation along the hexagonal [111] axis.

FIG. 1: (Color online) Helmholtz free mixing energy per site $f_{\text{mix}}$ of Ag$_{1-c}$Pd$_c$ at $T = 1$K, 20K, 50K, 100K, 200K (from up to down).

1 R. A. Johnson, Phys. Rev. B 41, 9717 (1990).
2 N. Takano, A. Yoshikawa, and F. Terasaki, Solid State Commun. 107, 213 (1998).
3 Z. W. Lu, S.-H. Wei, A. Zunger, S. Frota-Pessoa, and L. G. Ferreira, Phys. Rev. B 44, 512 (1991).
4 S. Müller and A. Zunger, Phys. Rev. Lett. 87, 165502 (2001).
5 S. Curtarolo, D. Morgan, and G. Ceder, Comput Coupling Phase Diagrams Thermochem. 29, 163 (2005).
6 A. V. Ruban, S. I. Simak, P. A. Korzhavyi, and B. Johansson, Phys. Rev. B 75, 054113 (2007).
7 A. Gonis, W. H. Butler, and G. M. Stocks, Phys. Rev. Lett. 50, 1482 (1983).
8 S. Takizawa, K. Terakura, and T. Mohri, Phys. Rev. B 39, 5792 (1989).
9 A. I. Abrikosov and H. L. Skriver, Phys. Rev. B 44, 512 (1991).
10 P. R. Weiss, Phys. Rev. 74, 1493 (1948).
11 We suppose here again, that each site has same coordination number.
12 H. S. Robertson, Statistical Thermophysics (Prentice-Hall, New Jersey, 1993).
13 T. Vojta and W. John, J. Phys.: Condens. Matter 5, 57 (1993).
14 T. Vojta, W. John and M. Sreiber, J. Phys.: Condens. Matter 5, 4989 (1993).
15 M. Ropo, K. Kokko, L. Vitos and J. Kollár, Phys. Rev. B 71, 45411 (2005).
16 L. Vitos, Computational Quantum Mechanics for Materials Engineers: The EMTO Method and Applications, Engineering Materials and Processes Series (Springer-Verlag, London, 2007).
17 L. Vitos, I. A. Abrikosov, and B. Johansson, Phys. Rev. Lett. 87, 156401 (2001).
18 P. Soven, Phys. Rev. 156, 809 (1967).
19 B. L. Györffy, Phys. Rev. B 5, 2382 (1972).
20 O. Redlich and A. T. Kister, Ind. Eng. Chem. 40, 345 (1948).
21 T. Hoshino, W. Schweika, R. Zeller, and P. H. Dederichs, Phys. Rev. B 47, 5106 (1993).
22 www.imprs-am.mpg.de/summerschool2003/skriver.pdf
23 E. Delczeg-Czirjak, et al., Unpublished.
24 R. Hultgren et al., Selected Values of the Thermodynamic Properties of Binary Alloys (American Society for Metals, Metals Park, Ohio, 1973).
FIG. 2: (Color online) Neighbor correlators of Ag$_n$Pd$_{1-n}$ at various temperatures $T = 1K, 20K, 50K, 100K, 200K$ (from up to down).