Temperature and particle size dependence of equilibrium order parameter of FePt

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First, second and third nearest neighbor pair mixing potentials for equiatomic FePt alloys were calculated from first principles by the Connolly-Williams method within the canonical cluster expansion formalism. It was demonstrated that the Connolly-Williams potentials (based on completely ordered states) and the Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA) potentials (based on completely disordered state) can be brought into very close correspondence to each other simply by increasing the magnitude of the strain-induced interactions added to the KKR-CPA potential. Using the mixing potentials obtained in this manner, the dependency of equilibrium L1$_0$ ordering on temperature was studied for bulk and for (approximately) spherical nanoparticles ranging in size from 2.5 to 6nm. The order parameter was calculated using Monte Carlo simulation and the analytical ring approximation. The calculated order-disorder temperature for bulk (1495-1514 K) was in relatively good agreement (4% error) with the experimental value (1572K). For nanoparticles of finite size, the (long range) order parameter changed continuously from unity to zero with increasing temperature. Rather than a discontinuity indicative of a phase transition, we obtained an inflection point in the order as a function of temperature. This inflection point occurred at a temperature below the bulk phase transition temperature and decreased as the particle size decreased. Our calculations predict that 3.5nm diameter particles in configurational equilibrium at 600°C (a typical annealing temperature for promoting L1$_0$ ordering) have an L1$_0$ order parameter of approximately 0.84 (compared to a maximum possible value equal to unity). According to our investigations, the experimental absence of (relatively) high L1$_0$ order in 3.5nm diameter nanoparticles annealed at 600°C or below is primarily a problem of kinetics rather than equilibrium.

I. INTRODUCTION

Self-assembled, monodispersed FePt nanoparticles are being intensively investigated for possible future application as an ultra-high density magnetic storage medium. In order to be useful as a storage medium, however, these particles, because of their extremely small volume, $V$, must have sufficiently high magnetic anisotropy, $K_u$, to withstand thermal fluctuations of the direction of magnetization. This requires values of the thermal stability factor, $(K_u V) / (k_B T)$, of approximately 50. The particles are usually produced by a "hot soap" process that yields a disordered f.c.c. solid solution alloy (e.g. Ref. 1). Such particles are not useful for information storage in the as-made state because they are paramagnetic at room temperature due to their low magnetic anisotropy.

Typically, the particles are annealed at a temperature $T \approx 600°C$ in order to induce an ordered L1$_0$ phase. The layered L1$_0$ phase is known from studies of bulk alloys to have an extremely high magnetic anisotropy ($K_u \approx 7 \times 10^6$ erg/cm$^3$). This value of magnetic anisotropy would provide a sufficiently large thermal stability factor to make 3.5nm diameter particles viable for information storage.

Unfortunately, it appears to be difficult to achieve a high degree of long range atomic order in FePt nanoparticles with $\lesssim 4$nm diameter by annealing at $T \lesssim 600°C$ (e.g. Ref. 2). One can consider two possible reasons for the fact that it has not been possible to obtain well ordered small particles. First, the observed order may be low because the particle is not in its equilibrium state due to the slow kinetics at low temperatures. Alternatively, the equilibrium order itself may be low even at relatively low temperatures because of the small size of nanoparticles. The latter explanation was suggested in Ref. 2. There, the order-disorder phase transition temperature was estimated to decrease with decrease of particle size. For particle sizes less than 1.5 nm in diameter, the phase transition temperature was found to be below the typical annealing temperature ($T \approx 600°C$). Therefore, particles of diameter less than 1.5 nm were predicted to have no long range order in their equilibrium state at 600°C. This explanation is in qualitative agreement with experiment. The difference between the experimental (4nm) and theoretical (1.5nm) critical size for disappearance of L1$_0$ order at 600°C was attributed to the neglect of nanoparticle surface effects.

From our point of view, however, the results obtained in Ref. 2 require verification because of the limitations of the theoretical models used in that study. Namely, the interatomic potentials in alloys usually are much more complicated and long-ranged than the nearest neighbor Lennard-Jones model that was used. In addition, the order-disorder phase transition temperature was estimated in Ref. 2 by comparing the free energies of completely ordered and completely disordered states; whereas in reality, the ordered state approaches (with increasing temperature) the phase transition point being not completely ordered. Also, the disordered state would be expected to approach the phase transition (with
decreasing temperature), not with a completely random atomic distribution but with an atomic distribution that has substantial short range order. Moreover, it is known that there is no formal phase transition in a finite system.

The aim of the present paper is to determine the reason for the low value observed experimentally for the L10 order parameter in small nanoparticles at typical annealing temperatures through the use of theoretical models that do not have the above-described limitations.

Presently, there are two main approaches for calculating effective atomic interactions (called mixing potentials in this paper) that determine the configurational behavior of atoms in an alloy. One is the Connolly-Williams method, which is based on the first principles calculation of the energies of a number of completely ordered structures. The second approach is based on the coherent potential approximation (CPA) for the completely disordered state (e.g. Ref. 10). In the present paper we utilize and compare both approaches. The first-principles calculations that we performed in order to implement the Connolly-Williams method were carried out in the generalized gradient approximation to density-functional theory, using the VASP program package. To obtain mixing potentials from the CPA we used data obtained within the Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA) in Ref. 16.

To study the temperature, concentration and size dependencies of equilibrium long-range order in FePt bulk and nanoparticles we used Monte Carlo simulation (utilizing the Metropolis algorithm) and the analytical ring approximation.

II. LATTICE GAS MODEL AND CLUSTER EXPANSION

We consider an Fe-Pt alloy in the framework of the two-component A-B lattice gas model (e.g. A=Pt, B=Fe). In this model, two types of atoms are distributed over the sites of a rigid crystal lattice. The atoms are allowed to be situated only at the crystal lattice sites and each site can be occupied by only one atom. The atoms interact through the lattice potentials and can exchange their positions according to Gibbs statistics. The lattice gas model is the most commonly used model for describing substitutional ordering in alloys (e.g. Refs. 10,21).

The configurational state of the lattice gas considered here can be defined by the set of configurational variables:

\[
 C^\alpha_R = \begin{cases} 
 1, & \text{if the site } R \text{ is occupied by an } \alpha \text{-type atom} \\
 0, & \text{otherwise} 
\end{cases},
\]

where \( \alpha = \text{A, B} \) and \( R \) is the site radius-vector. Because each site contains only one atom, we have

\[
 C^\alpha + C^B_R = 1 \Rightarrow C^B_R = 1 - C^\alpha_R.
\]

Thus any configurational state of the two-component lattice gas model (i.e. any particular distribution of atoms over the sites) can be determined by \( C^\alpha_R \) variables only.

The energy of any state can be expanded as (e.g. Sec. 2 in Ref. 21)

\[
 E = E_0 + \sum_{\alpha R} E^\alpha_R C^\alpha_R + \frac{1}{2} \sum_{\alpha_1 \alpha_2 R_1, R_2} E^{\alpha_1 \alpha_2}_{R_1, R_2} C_{R_1}^\alpha R_{2}^{\alpha},
\]

where \( E_0, E^\alpha_R \) and \( E^{\alpha_1 \alpha_2}_{R_1, R_2} \) are the coefficients of the energy expansion. \( E^{\alpha_1 \alpha_2}_{R_1, R_2} \) can be considered as pair interactions between two atoms of types \( \alpha_1 \) and \( \alpha_2 \) situated at \( R_1 \) and \( R_2 \) sites, respectively. Expression (3) is usually called a cluster expansion. In (3), the terms proportional to the powers of \( C^\alpha_R \) higher than second power are not taken into account. Terms corresponding to non-pair atomic interactions were found to be small in equiatomic FePt alloy (see discussion in Sec. III) so that we excluded them from the beginning.

By the use of (3), one can exclude \( C^B_R \) from (3) and get

\[
 E = V^{(0)} + \sum_{R_1} V^{(1)}_{R_1} C^A_{R_1} + \frac{1}{2} \sum_{R_1, R_2} V^{(2)}_{R_1, R_2} C^A_{R_1} R_{2}^{A},
\]

where \( V^{(i)} \) (\( i = 0, 1, 2 \)) we call mixing potentials (other names are "interchange energies" and "effective cluster interactions"):

\[
 V^{(1)}_{R_1} = E^A_{R_1} - E^B_{R_1} + \sum_{R_2} [E^{A, B}_{R_1, R_2} - E^{B, B}_{R_1, R_2}],
\]

\[
 V^{(2)}_{R_1, R_2} = E^{A, A}_{R_1, R_2} - 2 E^{A, B}_{R_1, R_2} + E^{B, B}_{R_1, R_2}.
\]

\( V^{(0)} \) is the energy of lattice gas with B atoms only. The knowledge of the mixing potentials is important because they determine the energetics of the lattice gas. A number of methods have been elaborated for calculation of the mixing potentials.

III. CONNOLLY-WILLIAMS METHOD

Within the Connolly-Williams method, the mixing potentials are assumed to have the symmetry of the disordered state, i.e. to be configurationally independent. Thus, \( V^{(1)}_{R_1} \) is independent of \( R \) and the pair mixing potential \( V^{(2)}_{R_1, R_2} \) depends only on the difference \( R_1 - R_2 \):

\[
 V^{(1)}_{R_1} = V^{(1)}_{R_1 - R_2}, \quad V^{(2)}_{R_1, R_2} = V^{(2)}_{R_1 - R_2}.
\]

The pair mixing potential \( V^{(2)}_{R_1, R_2} \) can be represented by its values \( V_s^{(2)} \) for different coordination shells:

\[
 V_s^{(2)} = V^{(2)}_{R_1}.
\]
where $R_s$ is the radius-vector connecting any given site with another site that belongs to the $s$-th coordination shell with respect to that given site. Generally, we define a coordination shell for a given site to be all of the sites that interact with a given site with the same value of the pair mixing potential.

Within the Connolly-Williams method, the energies $E_i$ ($i = 1, 2, \ldots, N_s$) of some $N_s$ structures (i.e., long-range ordered periodic atomic distributions sometimes called superstructures; for example Li$_3$O) are calculated by first principles methods. Writing Eq. (4) for each of those $N_s$ structures, one can get the following system of linear equations

$$
\begin{align*}
\varepsilon_i &= V^{(1)}c_i + \sum_{s=1}^{N_s} S_{is}V_s^{(2)} , \\
\end{align*}
$$

where

$$
\varepsilon_i = \frac{E_i - V^{(0)}}{N_i^A + N_i^B},
$$

$N_i^A$ and $N_i^B$ are the total numbers of A and B atoms in $i$-th structure, respectively, $S_{is}$ are the structural coefficients, and $c_i$ is the concentration of A atoms:

$$
c_i = N_i^A/(N_i^A + N_i^B).
$$

The energy $V^{(0)}$ of a pure B crystal is also calculated by first principles methods. So the problem is to find $N_s + 1$ unknown mixing potentials $V^{(1)}$ and $V_s^{(2)}$ ($s = 1, 2, \ldots, N_s$) that give the best fit [through Eq. (9)] to the energies $\varepsilon_i$ ($i = 1, 2, \ldots, N_s$) calculated by the first principles methods.

Usually, the choice of the structures to be used is random with a predisposition towards the well-known ones that are more easily calculated. It is preferable that the structures be experimentally observable for the alloy under consideration and that they correspond to the ground state or at least a low energy state (e.g., Ref. 25). However, since all configurations are possible for Eqs. (4) and (10), any convenient structure can be used for determination of the mixing potentials.

So, in contrast to the usual procedure, our criterion for the choice of the structures is only that they be linearly independent. By linear independence we mean that the main determinant of the system i.e., the determinant of the matrix $|\delta_{i,j}(c_i - S_{ij}) + S_{ij}|$ is not zero ($i, j = 1, 2, \ldots, N_s$; $\delta$ is the Kronecker delta). Among the linearly independent structures we chose those with less than twenty atoms per unit cell in order to reduce the cost of the first principles calculations. Note that all of the structures have the same composition (see below), there is only one ground state (if it is not degenerate) and the usual procedure of using only (or mainly) the ground states within the Connolly-Williams method is inapplicable. One may hypothesize that the use of non-ground states should expand the applicability of the resulting mixing potentials to higher temperatures.

In the present paper we mainly (except Figs. 9-12) study the Fe-Pt alloy close to equiatomic composition $c = 0.5$. Accordingly, we chose input structures to be of the same composition $c_i = 0.5$. The reason for doing so is the following. If we use structures of different compositions to find the mixing potentials, we imply that the mixing potentials are exactly the same for all compositions. However, the electronic structure of an alloy system generally depends strongly on composition. (For example, at low temperatures the FePt alloy shows a strong dependence of magnetic properties on composition: Fe$_3$Pt, FePt and FePt$_3$ are ferromagnetic, ferromagnetic and antiferromagnetic, respectively.) The mixing potentials are mainly determined by the electronic structure of the alloy and, therefore, one may expect a compositional dependence of the mixing potentials as well. For example, such a dependence of pair mixing potential was found numerically within KKR-CPA in Ref. 23. For such systems with strong compositional dependence of properties one may expect faster convergence of the Connolly-Williams method results with respect to increase of $N_s$ and $N_e$ when the considered structures are of the same composition. Such an approach corresponds to the canonical cluster expansion formalism and was applied e.g. in Ref. 25.

Note that the Connolly-Williams method is usually applied using structures of different compositions assuming compositional independence of mixing potentials (grand canonical cluster expansion formalism). In this approach, the compositional dependence of alloy properties (e.g., the asymmetry of the phase diagram with respect to $c = 0.5$) manifests itself through the presence of non-pair mixing potentials. In our approach the compositional dependence of alloy properties arises partly from the composition dependence of the mixing potentials. This approach is similar to that used in methods based on the study of the ordered state (e.g., CPA). Therefore, a direct comparison of Connolly-Williams and CPA potentials is possible (see below Sec. VI).

The first principles calculations were performed within the generalized gradient approximation to density-functional theory, using the VASP program package with mainly default settings. All calculations were spin polarized. The effect of lattice vibrations was omitted. All structures were totally relaxed including shape and volume relaxation of the unit cell as well as the individual displacements of atoms within the unit cell. The densities of $k$-points using the Monkhorst-Pack mesh in the corresponding full Brillouin zones were chosen to be similar for all considered structures and approximately equal $\pi/a, \pi/a, \pi/a$ (a is the f.c.c. lattice parameter), but the convergence of the results was checked to verify that it was sufficient in all cases. For the calculation of $\varepsilon_i$ [see Eq. (10)] for each structure we used the quantity $V^{(0)}$ (energy of pure Fe) calculated separately using the same parameters (both unit cell and VASP parameters) as for the corresponding structure. We believe that this approach diminished the error of the difference $E_i - V^{(0)}$ (and cor-
respectively of \( \varepsilon_i \) compared to the error of \( E_i \) and \( V^{(0)} \) themselves, due to the systematic cancelation of errors.

The L10 structure was included among the structures considered. In this case, after atom position relaxation, we obtained 3.848\( \AA \) and 3.771\( \AA \) for the \( a \) and \( c \) lattice parameters of the corresponding tetragonal lattice, respectively (\( c/a = 0.980 \)). For comparison the experimental values are 3.847\( \AA \) and 3.715\( \AA \) (\( c/a = 0.966 \)).

In addition, our calculated results showed the L10 ferromagnetic structure to be more stable (i.e. has lower energy) than the antiferromagnetic one in accordance with experiment. We believe that this good correspondence between theoretical and experimental results confirms the adequacy of our VASP first principles calculations.

The results of the application of our Connolly-Williams method to FePt are presented in Figs. 1-4 and Table. In Fig. 2 in analogy with Ref. 23, we present the dependencies of cross-validation (CV) and least-squares fitting (LSF) errors

\[
(CV)^2 = (23)^{-1} \sum_{i=1}^{23} (\varepsilon_i^{\text{VASP}} - \varepsilon_i^{\text{CW}})^2, \tag{12}
\]

\[
(LSF)^2 = (23)^{-1} \sum_{i=1}^{23} (\varepsilon_i^{\text{VASP}} - \varepsilon_i^{\text{CW}})^2 \tag{13}
\]

as well as of the phase transition temperature on \( N_s \).

In Eqs. (12), (13): \( \varepsilon_i^{\text{VASP}} \) (\( i = 1, 2, \ldots, 23 \)) correspond to the values obtained within the VASP code for 23 linearly independent structures (see Appendix A); \( \varepsilon_i^{\text{CW}} \) are obtained for those structures using the mixing potentials obtained by the Connolly-Williams method at \( N_s = 23 \); \( \varepsilon_i^{\text{CW}} \), are obtained for those structures using the mixing potentials obtained by the Connolly-Williams method at \( N_s = 22 \) when \( i \)-th structure is excluded from fitting. Such a CV error characterizes the predictive power of these Connolly-Williams potentials within the set of 23 structures.

In Fig. 3, the convergence of the results obtained by the Connolly-Williams method at \( N_s = 3 \) is verified with respect to an increase in the number, \( N_c \), of structures taken into account within the method. Up to 23 linearly independent structures (see Appendix A) were considered. Note that to achieve the rapid convergence shown in Fig. 3 it was important to begin with structures having the highest symmetries. Noting that the use of linearly independent structures guarantees that the good convergence (starting from \( N_c \approx 8 \)) is not caused by a simple similarity of structures.

In Fig. 4 we compare the values of \( \varepsilon_i - V^{(1)} \varepsilon_i \) [see Eqs. (10)] for each of the twenty three linearly independent structures (see Appendix A). The figure shows the values calculated both directly from first principles and by the use of the mixing potentials obtained by the Connolly-Williams method at \( N_s = 3, N_c = 23 \). The absolute differences between those two energies characterize the accuracy of Connolly-Williams fitting in the case of each structure. The average accuracy of 5.72% (8.63 meV) per one structure was obtained. In order to check the predictive power of these Connolly-Williams potentials outside the set of 23 structures, we also calculated the energies of five additional structures. This set of five structures includes all distinguishable (but not identical to the previous twenty three ones) equiatomic structures based on two-cubic unit cells in the f.c.c. crystal lattice (see Appendix A). The average accuracy of the Connolly-Williams potential for the five additional structures and for all 28 structures were obtained to be 7.60% (10.52 meV) and 6.06% (8.97 meV) per one structure, respectively. It is important that if we calculate the Connolly-Williams potentials using all 28 structures \( (N_s = 28) \) we obtain almost the same average accuracies of the energy fitting for the first 23, last five and all 28 structures: 5.92% (8.53 meV), 7.79% (10.36 meV) and 6.25% (8.85 meV) per one structure, respectively. Thus, one may conclude that the comparatively lower accuracy of fitting for the last five structures is not caused by not including them into the fitting set. Such a high predictive power confirms our choice of using only linearly independent (see above) structures in the Connolly-Williams method, because the last five structures in Fig. 4 are linearly dependent (but not identical) to the first twenty three structures. One may suppose that the use of additional linearly dependent structures in the Connolly-Williams method would simply impose extra weight factors for some of the initial structures.

The good convergence as a function of \( N_c \) shown in
Williams method at fixed $N$-value $46$ calculated as a function of the number of pair mixing potential values $N$ into account within the method.

FIG. 3: The values of pair mixing potential $V_s^{(2)}$ for seventeen coordination shells $(s = 1, 2, \ldots, 17)$ corresponding to the KKR-CPA method (KKR-CPA), strain-induced interactions (SI) at $L = -0.0294$, KKR-CPA method plus strain-induced interactions at $L = -0.0294$ (KKR-CPA+SI) (see Sec. III) as well as calculated by the Connolly-Williams method (CW) at $N_e = 3$, $N_e = 23$ (see Sec. III). See also Fig. 1. The cartesian coordinates of vector $R$ are given in $a/2$ units, where $a$ is the f.c.c. lattice parameter. Potential values are in meV units.

| Shell | $\mathbf{R}$ | $\mathbf{R}/a$ | KKR-CPA | SI | KKR-CPA+SI | CW |
|-------|---------------|----------------|--------|----|------------|----|
| 1     | 110           | 0.707          | 155.855| -9.879 | 175.976    | 87.69 |
| 2     | 200           | 1.000          | -2.997 | -2.484 | -5.481     | -39.46 |
| 3     | 211           | 1.225          | 12.413 | 0.326  | 12.739     | 15.85 |
| 4     | 220           | 1.414          | -5.714 | 1.173  | -4.541     |        |
| 5     | 310           | 1.581          | 1.727  | -0.724 | 1.003      |        |
| 6     | 322           | 1.732          | 1.214  | 0.091  | 1.304      |        |
| 7     | 321           | 1.871          | 0.907  | 0.133  | 1.040      |        |
| 8     | 400           | 2.000          | 0.974  | -0.053 | 0.921      |        |
| 9     | 411           | 2.121          | 0.147  | -0.188 | -0.041     |        |
| 10    | 420           | 2.236          | -0.050 | -0.209 | -0.258     |        |
| 11    | 332           | 2.345          | 0.015  | 0.030  | 0.045      |        |
| 12    | 422           | 2.449          | 0.099  | 0.060  | 0.160      |        |
| 13    | 431           | 2.550          | -0.075 | 0.074  | -0.001     |        |
| 14    | 510           |               | 0.030  | -0.058 | -0.028     |        |
| 15    | 521           | 2.739          | -0.006 | -0.073 | -0.079     |        |
| 16    | 440           | 2.828          | -0.042 | 0.163  | 0.121      |        |
| 17    | 433           | 2.915          | 0.008  | 0.019  | 0.027      |        |
| 18    | 530           |               | -0.008 | -0.058 | -0.066     |        |
| 19    | 442           | 3.000          | -0.007 | 0.023  | 0.016      |        |
| 20    | 600           |               | 0.000  | -0.037 | -0.037     |        |

Fig. 2 the high predictive power within and outside the set of 23 structures, the small CV and LSF errors of the Connolly-Williams fitting shown in Figs. 2-4 and the position of the local minimum of CV error as a function of the number of fitting parameters in Fig. 2 suggest that the neglect of nonpair mixing potentials and of pair mixing potentials outside three coordination shells (i.e. $N_e = 3$) as well as consideration of $N_e = 23$ linearly independent structures is sufficient to obtain adequate results within the Connolly-Williams method for the case considered here. The small difference between the experimental bulk order-disorder phase transition temperature and that obtained using these mixing potentials (see Fig. 2 and below Tab. III in Sec. VII) provides indirect evidence of adequacy of the potentials for equiatomic Fe-Pt. In Fig. 1 and Tab. I the pair mixing potential values obtained by the Connolly-Williams method at $N_e = 3$, $N_e = 23$ (four fitting parameters) are shown. Uniform weight factors were used in the fitting. We obtained also $V^{(1)} = 1.394$ eV.

Independent calculations within the KKR-CPA and the lattice-statics method also suggest that the atomic interaction tail outside the fourth coordination shell is weak (see below Sec. VII), despite the "$k \to 0$ nonanalyticity" of the Fourier transform of the corresponding pair mixing potential.
FIG. 4: The values of \( \varepsilon_i - V^{(1)}_c \) [see Eqs. (10-11)] for twenty eight equiatomic (\( c_i = 0.5 \)) structures calculated both directly from first principles and by the use of the mixing potentials obtained by the Connolly-Williams method (at \( N_e = 3, \ N_e = 23 \)). The differences between those two energies characterize the accuracy of Connolly-Williams fitting in the case of each structure. The first twenty three structures (see Appendix A) are linearly independent and they (and only they) were used in the Connolly-Williams method. The last five structures (right side of the vertical dashed line) correspond to all distinguishable (but not identical to the previous twenty three ones) equiatomic structures based on two-cubic unit cells in the f.c.c. crystal lattice (see Appendix A). Those five structures were not used in the Connolly-Williams fitting, but they were considered in order to assess the predictive power of the obtained Connolly-Williams potentials.

In Ref. 34 the Connolly-Williams method with structures of different concentrations was applied to FePt. Consideration was not limited to the ground state structures. One "hypothetical" phase L1\(_1\) was considered. The interchange model was restricted to two coordination shells of atomic pair interactions neglecting non-pair interactions. Only six structures were considered making the number of unknown potential parameters equal to the number of input parameters (energies of structures). The convergence of the results obtained by the Connolly-Williams method with respect to an increase in number of considered structures was not checked. Consideration of Fig. 3 indicates that for such a small number of structures convergence may not be achieved because of errors in the energy calculation. For all structures, the relaxation of the unit cell volume was performed in a way that neglected possible unit cell shape relaxation (resulting e.g. in its tetragonality) as well as neglecting the individual displacements of atoms within the unit cell. Using potentials calculated in this way, the phase transition temperature for equiatomic FePt bulk alloy was found to be 2070K, which is much higher than the experimental one \( \sim 1573K \).

In Ref. 35 the ratio \( V^{(2)}_2/V^{(2)}_1 = -0.729 \) was derived through the use of first principles calculations. This is different from the value \( V^{(2)}_2/V^{(2)}_1 = -0.45 \) obtained by the Connolly-Williams method used in the present paper.

It is difficult to determine the reason for this difference because details of the first principles calculations of Ref. 35 are not reported. It is possible that the elastic contribution to the mixing potential neglected in Ref. 35 is responsible for the difference. In Ref. 35 the value of \( V^{(2)}_1 = 96 \text{ meV} \) (in our designation) was fit by reproducing the experimental bulk phase transition temperature. This implies a value of the quantity \( V^{(2)}_2 \) of \( = -70 \text{ meV} \). For comparison, our Connolly-Williams potential values (see Tab. III) are very similar for the first coordination shell but almost a factor of two smaller for the second one. In addition, for the third shell, the Connolly-Williams potential is nonzero. Of course, the experimental bulk phase transition temperature is not reproduced perfectly by our set of Connolly-Williams mixing potentials which was obtained without fitting to experiment data (see below Tab. III in Sec. VII).

IV. L1\(_0\) PARALLEL ANTIPHASE DOMAINS

For the case of the L1\(_0\) structure, there is a possibility of creating parallel antiphase domains, i.e. the regions where the same L1\(_0\) structures are shifted with respect to one another by the distance \( a/2 \) along the z-axis perpendicular to the L1\(_0\) layers. The antiphase domains are usually created as a result of nucleation and growth of the L1\(_0\) structure in different places as the initially disordered sample is cooled below the order-disorder phase transition temperature. The antiphase boundaries (APB) between the antiphase domains contribute to the total energy making the existence of antiphase domains favorable or unfavorable depending on the sign of the antiphase boundary energy.

It is easy to show that such parallel APB energies vanish in the case of only nearest neighbor interactions. Thus, first principles calculation of parallel APB energies is important because it allows one to test the adequacy of the nearest neighbor interaction model for FePt. In addition, knowledge of the parallel APB energy is helpful for interpretation of Monte Carlo simulation results (see below Sec. VII) for the order parameter obtained by averaging in real space.

In order to estimate the parallel APB energies, we calculated the values of \( E_a, E_{2a} / E_{2a}, i.e. \) the total energies of the pure L1\(_0\) structure and of two structures composed of antiphase domains periodically repeated along the \( y \) direction with steps \( a \) and \( 2a \), respectively (corresponding to the structures 1-3 in Appendix A). The differences \( \delta E_a \) and \( \delta E_{2a} \):

\[
\delta E_a = E_a - E_0, \quad \delta E_{2a} = E_{2a} - E_0 \tag{14}
\]

can be considered as the total energies of a parallel APB in the corresponding two cases. The results of the calculations are presented in Tab. III. Note that, besides...
Table II: The energies $\delta E_a$ and $\delta E_{2a}$ of parallel APBs in the L1$_0$ structure in the cases of $a$ and $2a$ distance between parallel APBs, respectively. The values shown are per two atoms in one APB (in eV units) and were calculated by first principles using the VASP program package.

|                | Unrelaxed | Relaxed   |
|----------------|-----------|-----------|
| $\delta E_a$   | 0.223     | 0.213     |
| $\delta E_{2a}$| 0.213     | 0.198     |
| $\delta E_a - \delta E_{2a}$ | 9.80 $\times 10^{-3}$ | 1.59 $\times 10^{-2}$ |

The small difference between $\delta E_a$ and $\delta E_{2a}$, also contain some contribution from the interaction between parallel APBs. Such a contribution must decrease with increasing distance between parallel APBs. The small difference indicates that the interaction between parallel APBs in the two cases considered is small and short-ranged. It is somewhat larger in the relaxed case in accordance with the longer range of elastic interactions. The positiveness of $\delta E_a$ and $\delta E_{2a}$ indicates that parallel APBs are not energetically favorable. The nonzero values of $\delta E_a$ and $\delta E_{2a}$ mean that the nearest-neighbor interaction model is not adequate for a description of FePt alloy in accordance with results obtained in Sec. III.

V. KKR-CPA AND STRAIN-INDUCED INTERACTIONS

Elsewhere, detailed procedures have been described for calculating effective atomic interactions (pair mixing potentials) within the KKR-CPA methodology. KKR-CPA-based effective atomic interactions are determined from the response of the electronic structure of the high-temperature, disordered alloy to small amplitude concentration waves. The results obtained within KKR-CPA in Ref. 10 in the case of Fe$_{0.5}$Pt$_{0.5}$ alloy are presented in Fig. 1 and Tab. II.

From Fig. 1 and Tab. II one may conclude that the Connolly-Williams and KKR-CPA potentials (both corresponding to equiatomic concentration $c = 0.5$) are similar but not identical. In both, only the three first coordination shells are substantially different from zero. The signs of the potential values for the first three coordination shells are the same within both methods. However, the absolute value of the Connolly-Williams potential for the first coordination shell is considerably smaller than that of the KKR-CPA. For the second shell, the situation is opposite. One may attribute the difference between the Connolly-Williams and KKR-CPA potentials to the different structural and magnetic states used for the calculations: completely ordered ferromagnetic for the former and completely disordered paramagnetic for the latter.

For verification of the correspondence of both potentials to the real FePt alloy we calculated the bulk order-disorder phase transition temperature (within the ring approximation and by the Monte Carlo simulation) using both of the calculated mixing potentials. Then we compared the obtained values with the corresponding experimental one. The results are presented below in Tab. III.

One can see that Connolly-Williams and KKR-CPA potentials underestimate and overestimate the experimental phase transition temperature, respectively, by almost the same difference.

Within the KKR-CPA calculation, the nuclei were constrained to occupy ideal f.c.c. crystal lattice positions so the effect of inhomogeneous static atomic displacements is neglected. The homogeneous ones are taken into account by minimizing the alloy’s total energy with respect to the lattice parameter of the underlying lattice.) The inhomogeneous static atomic displacements are expected to be small for FePt alloy because of the small tetragonality obtained experimentally and theoretically (see e.g. above Sec. III). For verification, we calculated the corresponding strain-induced contribution to the pair mixing potential independently within the Khachatryan semiphenomenological theory based on the microscopic Matsubara-Kanzaki-Krivoglaz lattice-statics method. This approach allows us to take into account the anisotropy and discrete (atomic) structure of a crystal lattice in contrast with the macroscopic continuum theory of elasticity.

To calculate the strain-induced interactions, we used the expression derived in Ref. 38 for the Fourier transform of the dynamical matrix. Platinum and iron were chosen as solvent and solute, respectively. The pair mixing potential is independent of this choice since it is symmetrical with respect to interchange of A and B, see Eq. 10. For the calculations, we used the following numerical values: the mass of a Pt atom $M = 32.40 \times 10^{-26}$ kg; the lattice parameter $a_0 = 3.92$Å; phonon frequencies: longitudinal $\omega_L = 2\pi \times 5.80$ and transverse $\omega_T = 2\pi \times 3.84$ (all in $\text{rad s}^{-1}$); elastic constants of Pt: $C_{11} = 3.580$, $C_{12} = 2.536$, $C_{44} = 0.774$ (all in $10^{12}$ dyn/cm$^2$). The coefficient $L$ of linear dependence of alloy lattice parameter $a$ on the Fe concentration $c$,

$$a = a_0(1 + Lc), \quad L = \frac{1}{a_0} \frac{\partial a}{\partial c} \bigg|_{c=0},$$

was calculated as $L = -0.029$. The concentration interval used for the calculation of $L$ was chosen so that the Vegard rule is well fulfilled since it is a necessary condition of applicability of the Matsubara-Kanzaki-Krivoglaz lattice-statics method.

The corresponding results for the strain-induced interactions are presented in Fig. 1 and Tab. II. From them it follows that the strain-induced contribution to the pair mixing potentials is comparatively small as we expected.
The dependencies of the Fourier transform $V_k^{(2)} = \sum_{\mathbf{R}} V_{\mathbf{R}}^{(2)} \exp(i\mathbf{k}\mathbf{R})$ of pair mixing potential $V_{\mathbf{R}}^{(2)}$ on the wavevector along the high-symmetry direction within the corresponding first Brillouin zone. The three cases correspond to (1) the pair mixing potentials obtained by the Connolly-Williams method (CW) at $N_c = 3, N_c = 23$ (see Sec. III) (2) pair mixing potentials obtained within the KKR-CPA and (3) KKR-CPA plus strain-induced interactions (KKR-CPA+SI) at $L = -0.0294; -0.0025$ (see Sec. III). The big bold point and triangle correspond to $V_{\mathbf{R}}^{(2)}$ in two cases of taking into account the strain-induced interactions, when the Fourier transform demonstrates nonanalitycity.

The addition of this contribution to the KKR-CPA potential decreases the corresponding phase transition temperature so that it is very close to the experimental one (see Tab. III).

From Fig. 1 and Tab. II one can also see that the addition of the strain-induced contribution to the KKR-CPA pair mixing potential moves it toward the Connolly-Williams potential values. To emphasize this effect, we increased the absolute value of the coefficient $L$ from 0.0294 to 0.0025 (thus artificially increasing the strain-induced interactions) in order to bring the KKR-CPA plus strain-induced potential as close to the Connolly-Williams one as possible. The same tendency is observed in the Fourier transforms of the corresponding pair mixing potentials (see Fig. 5). One may conclude that the mixing potential calculated for the disordered state (KKR-CPA) can be brought into close agreement with the mixing potential based on the completely ordered states (Connolly-Williams method) simply by increasing the magnitude of the strain-induced interactions (which is proportional to $L^2$). Perhaps such an increase of the strain-induced interactions roughly describes the dependence of mixing potential on the order parameter (configurational excitations of the electronic structure).

Note from Tab. III that the phase transition temperature corresponding to the KKR-CPA potential plus the artificially increased strain-induced interactions is much lower than the experimental one. This may be explained by the roughness of our approach. Namely, by bringing the KKR-CPA $V_k^{(2)}$ to the Connolly-Williams one in the vicinity of $G$ point (where the difference between them is largest), we may cause too large an error in $V_k^{(2)}$ in the vicinity of $X$ point, which is mainly responsible for the phase transition because of minimum of $V_k^{(2)}$ there (see Fig. 5).

From Fig. 1 and Tab. II it follows that the strain-induced potential is of short range despite the $"k \to 0$ nonanalitycity" of its Fourier transform. One may consider this fact as an additional proof of correctness of our application of the Connolly-Williams method in Sec. III using the short range pair mixing potential.

Below, in our Monte Carlo simulation of finite small systems, we exclusively used mixing potentials obtained by the Connolly-Williams method. We did so because the most interesting (for the aim of the present paper) temperature region corresponds to the highly ordered state. For this reason, we expect that the Connolly-Williams potentials which are based on the completely ordered state should work better in that region than the KKR-CPA potentials which are based on the completely disordered state.

In Ref. 45 the values of pair mixing potentials for the FePt bulk alloy were obtained within the tight binding linear orbital method. For $c = 0.5$, the values for the second and fourth coordination shell mixing potentials are close to the corresponding KKR-CPA ones from Ref. 17 but they are approximately a factor of two smaller for the first and third shells. Order-disorder transition temperatures of 662K, 816K, and 435K were obtained by us for $c = 0.25, c = 0.50,$ and $c = 0.75$, respectively, using these potentials within the ring approximation. These transition temperatures are much lower than the experimental ones (1087K, 1572K, and 1622K, respectively). The corresponding transition temperatures calculated in Ref. 45 are not so different from the experimental ones because the mean-field approximation, which usually overestimates the transition temperature, was used. The magnitude of the discrepancy with experiment was underestimated also because an old value for the transition temperature at $c = 0.75$ from Ref. 17 was used for comparison.

VI. MONTE CARLO SIMULATION

For the Monte Carlo simulations we utilized the standard Metropolis algorithm. We applied free and periodic boundary conditions for the cases of spherical nanoparticles and parallelepipeds, respectively.

To obtain a rapid approach to the equilibrium state, which is the subject of this paper, the starting configuration for each temperature was chosen to be the completely ordered one. We also used simplified kinetics in
our Monte Carlo simulation. Namely, we allowed any two randomly chosen atoms (not only nearest neighbors) to exchange their positions without an additional diffusion barrier.

The absence of a monotonic change of mean values of all quantities being calculated in the Monte Carlo simulation was chosen as a criterion for the achievement of an equilibrium state. To fulfill such a criterion, it was generally necessary to perform 1000 - 20000 Monte Carlo steps (i.e. the interchange of two atoms chosen at random) per site. After the equilibrium state was achieved, each calculated quantity was averaged for subsequent Monte Carlo steps. When the oscillation amplitudes of such averages (considered as a function of the number of Monte Carlo steps performed) became less than 5% of the absolute value of the corresponding average during the last 10% of steps (from the total number of steps carried out at an equilibrium state), the values of the averages calculated at the last Monte Carlo step were accepted as equilibrium ones.

We define the equilibrium L1₀ order parameter η as the statistical average of the maximum value among three absolute values of "directional" order parameters ηₓ, ηᵧ, ηz:

\[ \eta = \max\{|\eta_x|, |\eta_y|, |\eta_z|\} \]  \hspace{1cm} (16)

where \( \eta_i \) \( (i = x, y, z) \) is defined as the difference between the Fe atom concentrations at odd and even crystal planes perpendicular to \( i \)-th direction, \( \langle \ldots \rangle_{\text{MC}} \) is the statistical average over the Monte Carlo steps. We chose this definition of \( \eta \) because of the equivalence by symmetry of the \( x, y \), and \( z \) directions of L1₀ order. In addition, one can obtain an equivalent structure (at \( c = 0.5 \)) by changing the sign of \( \eta_i \), which results in the exchange of Fe and Pt atoms producing a configuration that is equivalent by symmetry to the original one. During Monte Carlo simulation, we observed fluctuations that cause transformations between these equivalent states (i.e. fluctuations in the sign and direction of \( \eta \), see Figs. 3-7). This is in addition to the usual statistical fluctuations within one such state. The L1₀ order parameter \( \eta \), defined in Eq. (16), takes into account the fluctuation induced transformations between the equivalent states. Note that because of the above-discussed symmetry equivalence, we obtain \( \langle \eta_i \rangle_{\text{MC}} = 0 \) for any \( i = x, y, z \) at any temperature, when the statistical average is taken over a sufficiently large number of Monte Carlo steps. Note that in Ref. 35 an order parameter similar to Eq. (16) was introduced for the same reasons.

Usually during Monte Carlo simulation we observed one of the "directional" order parameters to be much larger than other two (see e.g. Figs. 3-7). This means that the presence of perpendicular anti-phase domains is not favorable. Examination of the atomic arrangements within the Monte Carlo simulation showed no evidence of parallel anti-phase boundaries such as those discussed in Sec. IV. The absence of anti-phase domains confirms the validity of our definition of the equilibrium L1₀ order parameter in Eq. (16).

Note that even with our simplified kinetics (see above Sec. IV), we observed a slowing down problem in approaching the equilibrium ordered state at low temperatures. For example, in Fig. 4 one can see that, for a long time, the nanoparticle can be in a metastable state with order parameter (\( \sim 0.6 \)) lower than that (\( \sim 0.8 \)) in the equilibrium state.

![FIG. 6](image-url) The dependence of the FePt L1₀ order parameters on Monte Carlo steps during averaging in the equilibrium state during simulation of a spherical nanoparticle with diameter \( d = 3.0 \text{ nm} \) (see Tab. IV) at temperature \( T = 1100 \text{ K} \). \( \eta_x, \eta_y, \eta_z \) are the "directional" order parameters (see text), \( \eta \) is defined in Eq. (16).

![FIG. 7](image-url) The same as in Fig. 6 but for the "directional" order parameters as the spherical nanoparticle with diameter \( d = 3.0 \text{ nm} \) (see Tab. IV) approaches its equilibrium state at temperature \( T = 800 \text{ K} \).
VII. BULK PHASE TRANSITION

To obtain an additional verification of the calculated values of mixing potential, we calculated the order-disorder phase transition temperature in the bulk FePt equiatomic alloy using these values. To do so, we calculated the temperature dependence of the FePt equilibrium Li$_0$ order parameter $\overline{\eta}$ for bulk ("bulk") as well as by Monte Carlo simulation for parallelepiped ("ppd") samples containing $N = 20^3$, $40^3$, and $60^3$ atoms and the spherical ("sph") nanoparticle with $d = 5.94\text{nm}$ diameter (see Tab. IV) at (or near) equiatomic concentration $c = 0.5$. The results are presented in Fig. 8.

From Fig. 8 one may conclude the following. The ring approximation (which exactly corresponds to bulk, i.e. to an infinite sample) clearly shows a phase transition temperature at which the order parameter $\overline{\eta}$ drops to zero. Strictly speaking, in all the cases considered here of finite size samples (sphere and parallelepipeds) there is no phase transition in accordance with a general theorem. The order parameter $\overline{\eta}$ continuously changes from unity to zero with increasing temperature and instead of a phase transition we obtain an inflection point in the $\overline{\eta}(T)$ curve. In the case of the parallelepiped with $60^3 = 216000$ atoms, the inflection point is very similar to the phase transition. Comparing the three curves for parallelepipeds of different sizes one can imagine that the inflection point transforms into a phase transition in the limit of infinite size. The position of the inflection point is often used to approximate the bulk phase transition point in Monte Carlo simulations of finite size samples.

According to our calculations, the inflection point corresponding to the largest parallelepiped simulation can be considered to be a good estimate for the phase transition within the Monte carlo method. We plotted the temperature of the inflection point, $T_N$, as a function of $N^{-1/2}$ and observed the limiting value as $N^{-1/2} \to 0$. This extrapolation of $T_N$ to $N \to \infty$ hardly differs from the temperature of the inflection point for $N = 60^3$.

From Fig. 8 it follows that Monte Carlo simulation for parallelepipeds with periodic boundary conditions ("no surface") is much more appropriate to the bulk behavior than Monte Carlo simulation for the spherical nanoparticle with free boundary conditions. The number of particles $N = 20^3 = 8000$ in the smallest parallelepiped considered is very close to the number $N = 8007$ of particles in the spherical nanoparticle (see below Tab. IV). This large difference in Monte Carlo simulation between parallelepiped and sphere is caused by the difference in shape and boundary conditions.

| $V_s^{(2)}$ | $T_0$ (K) |
|------------|----------|
| EXPERIMENT | 1572     |
| CW         | 1495(ring), 1514(MC) |
| KKR-CPA    | 1610(ring) |
| KKR-CPA+SI (L = 0.0294) | 1552(ring) |
| KKR-CPA+SI (L = 0.0925) | 997(ring) |

The temperatures, 1495 K and 1514 K, estimated for the phase transition within the analytical ring approximation and Monte Carlo simulation, respectively, are in close correspondence to the experimental 1572 K. This 4% error demonstrates the adequacy of the mixing potential values at $c = 0.5$ calculated from first principles (i.e. without a fitting to experimental data).

In order to test the applicability of these values over the entire concentration interval, we calculated the order-disorder phase transition temperature as a function of concentration within the analytical ring approximation using the mixing potential calculated for $c = 0.5$. The corresponding results together with experimental ones are presented in Fig. 9 (see also Fig. 10). From this figure one may conclude that the equiatomic mixing potential is only valid in the vicinity of $c = 0.5$. Outside this vicinity it is necessary to use different mixing potentials. The asymmetry of experimental phase diagram with respect to $c = 0.5$ implies that the mixing potentials should be concentration dependent and/or nonpair. According to our canonical cluster expansion formalism, within the Connolly-Williams method one should calculate the
mixing potentials at any given concentration using structures with the same (or close) compositions. Within the KKR-CPA, the concentration dependence of mixing potentials is obtained naturally.

VIII. NANOPARTICLE SIMULATION

The mixing potentials calculated in Sec. III by the Connolly-Williams method were used for Monte Carlo simulations of the temperature dependence of the equilibrium L10 order parameter of spherical FePt nanoparticles with diameters of 5.94nm, 3.5nm, 3.0nm, and 2.5nm. In all cases the compositions are close to c = 0.5. The characteristics of those nanoparticles are listed in Tab. IV.

Note that the starting configuration for all cases considered was chosen to be a completely ordered one with an L10 order parameter of unity. The deviations of concentration from equiatomic c = 0.5 are due to the finite sizes and spherical shape of the nanoparticles.

The results of the simulations are presented in Fig. 11. For spherical nanoparticles, the tendencies in the behavior of order parameter are the same as in case of parallelepipeds (see above Sec. VII). Namely, in case of...
finite size particles, instead of a phase transition point (see bulk curve) there is an inflection point. The smaller the particle size the smoother the \( \bar{\eta}(T) \) curve, the less order parameter at low temperatures (below and somewhat above the inflection point) and the higher the order parameter at high temperatures (well above the inflection point). The inflection point temperature decreases with decrease of particle size. Note that in Ref. 13 the same tendencies were observed but the position of the heat capacity maximum was interpreted as a phase transition point. Such an interpretation should be very approximate in case of small finite systems because there is no formal phase transition in a finite system. The same tendencies as in Fig. 11 were observed in Monte Carlo simulation of Cu3Au nanoparticles in Ref. 49.

Our calculations predict, for example, that 3.5nm diameter particles in configurational equilibrium at 600°C would have an order parameter \( \bar{\eta} = 0.84 \) compared to a maximum possible value of unity (see Tab. IV, and Fig. 2). Therefore, annealing at 600°C will not yield perfect order for 3.5nm diameter particles. Approximately 17% of the atoms will be on the wrong sublattices, even in equilibrium. The corresponding dispersion of \( \eta \) due to the thermodynamic fluctuations is comparatively small (e.g. 2.5% for \( d = 3.5, T = 600^\circ \text{C} \), see Tab. IV).

The "tail" of the order parameter at high temperatures in Fig. 11 is a consequence of thermodynamic fluctuations of the order parameter. The asymptotic behavior of the dispersion of such fluctuations can be estimated as \( \sim 1/\sqrt{N} \) (\( N \) is the number of atoms). So the value of the high temperature "tail" of the order parameter increases with decreasing particle size. Note that we define the order parameter as in Eq. 10, taking into account the fact that two configurations with different signs of the order parameter are physically identical.

Experimentally, nanoparticles are created with some dispersion in the concentration. Therefore it is important to know the concentration dependence of the order parameter. We studied this dependency for the cases of bulk and spherical nanoparticles of different diameters at fixed temperature \( T = 600^\circ \text{C} \). The corresponding results are presented in Fig. 12. At each concentration we present the equilibrium order parameter value so that near concentrations \( c = 0.5 \) and \( c = 0.25; 0.75 \) the curves correspond to L10 and L12 order parameters, respectively.

From Fig. 12 it follows that for small FePt nanoparticles we observe an asymmetry in the concentration dependence of the order parameter with respect to equiatomic \( c = 0.5 \). This asymmetry is a consequence of the finite size of nanoparticles. It should be emphasized that for the calculation of order parameters in Fig. 12 at each concentration we used the same pair mixing potentials as at \( c = 0.5 \) that results in a symmetric order parameter for case of bulk. The concentration dependence of mixing potentials and/or appearance of non-pair mixing potentials at \( c \neq 0.5 \) can make the bulk curve asymmetric[26] and make an additional contribution to the asymmetry for finite particles observed in Fig. 12.

One should consider the results in Fig. 12 to be more approximate the further they are from \( c = 0.5 \).

**IX. SURFACE EFFECTS**

In our study, we have used mixing potentials obtained for infinite bulk alloys and free boundary conditions to simulate the equilibrium configuration of finite size particles. The presence of the surface will change the atomic potentials in the near-surface region compared to bulk potentials. This change may result in surface segregation, leading, for example, to the tendency of Fe or Pt atoms to be preferably situated at the surface. In general, surface segregation should decrease the total L10 order parameter in nanoparticles, because the L10 order will be reduced at the surface. The surface effect on the order will depend on the ratio of depth of surface segregation to nanoparticle size.

Analytical estimation of such surface effects is not straightforward and will be done elsewhere[26]. Here we only describe the source of the asymmetry observed in Fig. 12. Namely, it is observed that in the presence of a free surface the Connolly-Williams bulk mixing potentials result in weak segregation of Fe atoms to the surface. This causes a depletion of Fe in the interior of the nanoparticle. Thus the effective concentration of Fe atoms within the nanoparticle but outside the surface segregation region will be less than one half. Therefore...
it is necessary to add Fe atoms to the interior of the nanoparticle to achieve equiatomic composition outside the segregating surface and accordingly to achieve the maximum $L_10$ order in that region. That is why the maximum of the $L_10$ order parameter lies on the Fe-rich side of equiatomic composition in Fig. 12. A similar effect (but for the pseudo phase transition temperature in finite systems) was observed in Ref. 33 for the case in which a strong segregation potential leading to the segregation of Pt to the surface was introduced during Monte Carlo simulation. That additional potential also results in a decrease of total order parameter in accordance with our description above.

For nanoparticles chemically synthesized by methods such as the "hot soap process", the problem of the effect of the surface on the interatomic exchange potentials is even more complicated because these nanoparticles are likely to have unknown atoms and molecules attached to their surfaces. It should also be noted that truncation of the mixing potentials at a surface is an uncontrolled approximation. The fact that our simulations yield segregation of Fe to the surface should not be taken as evidence that this would happen for a real nanoparticle.

**X. CONCLUSIONS AND DISCUSSION**

In the present paper, the pair mixing potentials (which determine the alloy configurational behavior) were calculated up to the third coordination shell for equiatomic FePt alloys from first principles using the Connolly-Williams method (Sec. IV). It was shown that the application of this method does not necessarily lead to significant non-pair interactions if all of the structures employed in the Connolly-Williams method correspond to the same composition (canonical cluster expansion formalism). The mixing potential was also calculated by adding the strain-induced part of the interactions to mixing potentials obtained from the KKR-CPA approach of Ref. 14 (Sec. V). The application of the Connolly-Williams method at fixed composition allowed the direct comparison of these potentials with those obtained from the KKR-CPA (plus strain-induced part). The mixing potentials are shown to be similar with both giving values for the order-disorder phase transition very close to the experimental one. It was demonstrated that the Connolly-Williams potentials (based on completely ordered states) and the KKR-CPA potentials (corresponding to completely disordered state) can be brought into very close correspondence to each other simply by increasing the magnitude of the strain-induced interactions added to KKR-CPA potential (Sec. VI).

It should be emphasized that it was not clear a priori that either the Connolly-Williams method or the CPA approach could be trusted for a system as complicated as FePt. Magnetic alloys are problematic for the Connolly-Williams method because the mixing potentials are strongly dependent on the magnetic state of the system. Thus the chemical order and magnetic structure are expected to be intimately related. On the other hand the CPA approach is based on concentration fluctuations in a hypothetical high temperature disordered state. We consider the fact that both methods are able to approximate the order-disorder temperature well without adjustable parameters and that the mixing potentials derived from the two approaches are rather similar to be a remarkable result.

It was shown by first-principles calculations that parallel $L_10$ antiphase boundaries are not energetically favorable (Sec. IV). This fact demonstrates the inapplicability of the nearest neighbor interaction model in accordance with Connolly-Williams and KKR-CPA results. The absence of parallel $L_10$ antiphase boundaries was confirmed by Monte Carlo simulation using the Connolly-Williams potential (Secs. VII VIII).

In Secs. VII VIII the mixing potentials obtained by the Connolly-Williams method were used to investigate the dependence of equilibrium $L_10$ ordering on temperature for bulk and for spherical nanoparticles with diameters of 5.94nm, 3.5nm, 3.0nm and 2.5nm. These calculations used both Monte Carlo simulation and the analytical ring approximation. The calculated order-disorder temperature for bulk (1495-1514 K) was in relatively good agreement (4% error) with the experimental value (1572K). For nanoparticles of finite size, the (long range) order parameter changed continuously from unity to finite asymptotic values with increasing temperature. The nonzero asymptotic values are a consequence of thermodynamic fluctuations of the order parameter and are proportional to $1/\sqrt{N}$ where $N$ is the number of atoms in a sample. Rather than a discontinuity indicative of a phase transition we obtained an inflection point (a precursor of a phase transition at large size) in the $L_10$ order as a function of temperature. This inflection point occurred at a temperature below the bulk phase transition temperature and which decreased as the particle size decreased.

According to our investigations, the experimental absence of (relatively) high order in nanoparticles below 600°C is primarily a kinetic problem rather than an equilibrium one. For example, our calculations predict that 3.5nm diameter particles in configurational equilibrium at 600°C (a typical annealing temperature for promoting $L_10$ ordering) have an $L_10$ order parameter of 0.84 (compared to a maximum possible value equal to unity). It should be noted that to rapidly obtain the correct equilibrium state, we used simplified kinetics in our Monte Carlo simulation. Namely, we allowed any two randomly chosen atoms to exchange their positions without an additional diffusion barrier. In a real alloy, the main mechanism of atomic diffusion is much slower because it consists of the exchange of the positions of atoms and neighboring vacancies through energy barriers. Moreover, at each temperature we started the simulation from the completely ordered state, whereas the actual nanoparticles are initially prepared in disordered state and transformation from the disordered to the ordered state may be
much slower than the reverse one, especially at low temperatures. Nevertheless, even with our simplified kinetics, we observed a slowing down problem in approaching the equilibrium ordered state at low temperatures. In real nanoparticles this problem must be much worse. Kinetic acceleration methods such as irradiation and/or addition of other types of atoms may be useful in accelerating the formation of long range order. Harrell et al. have observed ordering on annealing at temperatures somewhat below 400°C by adding Ag or Au to the particles in the synthesis step. However, it appears that this ordering is also accompanied by agglomeration and sintering of the particles. It should be emphasized that all of the results presented in this paper correspond to equilibrium states and are, therefore, independent of the particular kinetic pathways that lead to these states.

In Sec. VIII it was demonstrated that for small finite samples even for a composition independent, pair mixing potential one obtains an asymmetric order parameter as a function of composition with respect to equiatomic compositions. In particular, for FePt nanoparticles, if we neglect the effect of the surface on the mixing potentials, the maximum of the $L_1^\text{cub}(1)$ order parameter as a function of composition with respect to equiatomic composition is shifted from $c=0.5$ toward the Fe rich region. The connection of such an asymmetry with surface segregation is discussed in Sec. IX.

XI. ACKNOWLEDGMENTS

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APPENDIX A: DEFINITION OF STRUCTURES

The present appendix (Tab. V and Subsecs. 1-28) defines the structures used in this paper. Unit cell basis vectors are given in Cartesian coordinates in units of the fcc lattice parameter. The Cartesian axes are directed along the edges of the fcc cube. The third unit cell basis vector is perpendicular to the first and second ones for all structures. All of the structures have equiatomic composition $c=0.5$. The atom positions in the tables are before relaxation. In addition to numbering, we also include the structure designations that we used during our calculations. For the first, second and twenty fourth structures we put also the designations known in the literature ("L1^cub", "CH(40)" and "Z2", respectively). The first 23 structures are linearly independent and were used in the Connolly-Williams method in Sec. III. The rest 5 structures are linearly dependent (but not identical) to the first 23 ones. They were considered in order to check the predictive power of the Connolly-Williams potentials.

TABLE V: The characteristics of the structures used in the paper. $i$ is the structure number, $N_{\text{u.c.}}^{AB}$, is the total number of atoms in the unit cell of structure. $E_{\text{u.c.}}$ is the energy of structure per its unit cell (as obtained from VASP calculations), $V_{\text{u.c.}}^{(0)}$ is the energy (per unit cell) of the structure with the same unit cell but with Fe atoms only (see Sec. III). $s_i$ are the structural coefficients $(i=1,2,..,8)$ in the Connolly-Williams system of equations (9). Note that the values of $s_i$ [see Eqs. (9)-(10)] can be determined from this table as $s_i = (E_{\text{u.c.}} - V_{\text{u.c.}}^{(0)})/N_{\text{u.c.}}^{AB}$, where the values on the right side of this equation correspond to the $i$-th structure.

| $i$ | $N_{\text{u.c.}}^{AB}$ | $V_{\text{u.c.}}^{(0)}$ | $E_{\text{u.c.}}$ | $s_i \times N_{\text{u.c.}}^{AB}$ |
|-----|-----------------|-----------------|-----------------|-----------------|
| 1   | 16              | -129.0729       | -117.0299       | 16 24 32 48 32 32 64 24 |
| 2   | -116.1764       | 16 16 64 16 16 32 0 128 24 |
| 3   | -116.6366       | 16 20 48 32 32 32 64 16 96 16 |
| 4   | -114.5503       | 40 20 64 32 64 16 96 16 |
| 5   | -114.9625       | 34 20 60 32 54 16 92 18 |
| 6   | -114.6047       | 36 20 64 32 56 16 92 16 |
| 7   | 16              | -128.9796       | -115.4659       | 27 14 38 24 54 8 76 24 |
| 8   | -115.3484       | 28 14 40 16 56 8 80 24 |
| 9   | -145.2008       | 18 22 44 42 36 28 88 23 |
| 10  | -130.8094       | 22 23 40 42 44 28 84 23 |
| 11  | -131.0869       | 20 23 44 42 42 28 84 23 |
| 12  | -130.6305       | -72.2655        | 10 9 26 12 34 8 66 9 |
| 13  | -57.1224        | 18 8 28 12 20 8 40 4 |
| 14  | -57.7453        | 13 6 26 10 22 12 44 8 |
| 15  | -4.08363        | -43.0543        | 12 5 16 8 12 8 32 5 |
| 16  | -96.7403        | -85.1600        | 30 14 52 24 44 16 80 10 |
| 17  | -85.7956        | 25 12 46 20 38 16 72 10 |
| 18  | -96.7380        | -86.9505        | 16 10 32 16 40 16 80 10 |
| 19  | -96.7780        | -86.6918        | 20 10 30 18 38 8 58 14 |
| 20  | -64.5403        | -58.1203        | 10 8 20 12 28 8 56 4 |
| 21  | -161.2637       | -144.2564       | 35 18 47 24 74 8 93 26 |
| 22  | -144.1195       | 36 18 46 22 76 6 94 26 |
| 23  | -129.0066       | -115.4983       | 28 14 38 22 54 8 76 20 |
| 24  | -64.5283        | -57.6927        | 16 8 16 8 32 0 32 12 |
| 25  | -57.8895        | 12 10 16 16 24 8 32 12 |
| 26  | -57.7018        | 12 8 24 8 24 0 48 12 |
| 27  | -57.1095        | 10 10 20 16 20 8 40 12 |
| 28  | -57.2748        | 8 10 24 16 16 8 48 12 |

1. 4cub(1), $L_1^\text{cub}$

Unit cell basis vectors Cartesian coordinates: $(1,0,0,0,0,0), (0,1,0,0,0,0), (0,0,0,0,4,0)$.

Atomic Cartesian coordinates:

A: $(0,0,0,0,0,0), (0,5,0,5,0,0), (0,0,0,0,1,0), (0,5,0,5,1,0), (0,0,0,0,2,0), (0,5,0,5,2,0), (0,0,0,0,3,0), (0,5,0,5,3,0)$;

B: $(0,5,0,0,0,5), (0,0,5,0,5), (0,5,0,0,1,5)$,
2. 4cub(2), APB(1), CH(40)

Unit cell basis vectors Cartesian coordinates:
(1.0,0.0,0.0), (0.0,1.0,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.5,0.0), (0.0,0.5,0.5),
(0.5,0.0,0.5), (0.0,0.0,0.5), (0.5,0.0,0.5),
(0.0,0.5,0.5), (0.5,0.5,0.5).

3. 4cub(3), APB(2)

Unit cell basis vectors Cartesian coordinates:
(1.0,0.0,0.0), (0.0,1.0,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.5,0.0), (0.0,0.5,0.5),
(0.5,0.0,0.5), (0.0,0.0,0.5), (0.5,0.0,0.5),
(0.0,0.5,0.5), (0.5,0.5,0.5).

4. 4cub(4)

Unit cell basis vectors Cartesian coordinates:
(1.0,0.0,0.0), (0.0,1.0,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.5,0.0), (0.0,0.5,0.5),
(0.5,0.0,0.5), (0.0,0.0,0.5), (0.5,0.0,0.5),
(0.0,0.5,0.5), (0.5,0.5,0.5).

5. 4cub(5)

Unit cell basis vectors Cartesian coordinates:
(1.0,0.0,0.0), (0.0,1.0,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.5,0.0), (0.0,0.5,0.5),
(0.5,0.0,0.5), (0.0,0.0,0.5), (0.5,0.0,0.5),
(0.0,0.5,0.5), (0.5,0.5,0.5).

6. 4cub(6)

Unit cell basis vectors Cartesian coordinates:
(1.0,0.0,0.0), (0.0,1.0,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.5,0.0), (0.5,0.0,0.5),
(0.0,0.0,0.5), (0.5,0.0,0.5), (0.0,0.0,0.5),
(0.5,0.5,0.5), (0.0,0.5,0.5).

7. 4ppd1-2pl(1)

Unit cell basis vectors Cartesian coordinates:
(1.0,-1.0,0.0), (1.0,1.0,0.0), (0.0,0.0,2.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,-0.5,0.0), (0.5,0.5,0.0),
(1.0,0.0,0.0), (0.5,0.0,0.5), (1.0,-0.5,0.5),
(1.0,0.0,0.5), (0.5,0.0,0.5).

8. 4ppd1-2pl(2)

Unit cell basis vectors Cartesian coordinates:
(1.0,-1.0,0.0), (1.0,1.0,0.0), (0.0,0.0,2.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,-0.5,0.0), (0.5,0.5,0.0),
(1.0,0.0,0.0), (0.5,0.0,0.5), (1.0,-0.5,0.5),
(1.0,0.0,0.5), (0.5,0.0,0.5).

9. 9ppd1-1pl(1)

Unit cell basis vectors Cartesian coordinates:
(1.5,-1.5,0.0), (1.5,1.5,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,-0.5,0.0), (1.0,-1.0,0.0),
(0.5,0.5,0.0), (1.0,0.0,0.0), (1.5,0.0,0.0),
(1.5,0.0,0.5), (2.0,0.0,0.5),
(1.0,0.5,0.5), (1.5,0.0,0.5), (2.0,0.5,0.5),
(1.0,1.0,0.5), (1.5,1.0,0.5).

10. 9ppd1-1pl(2)

Unit cell basis vectors Cartesian coordinates:
(1.5,-1.5,0.0), (1.5,1.5,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,-0.5,0.0), (1.0,-1.0,0.0),
(0.5,0.5,0.0), (1.0,0.0,0.0), (1.5,-0.5,0.0),
(1.5,0.5,0.0), (1.0,-0.5,0.5);
B: (2.0,0.0,0.0), (0.5,0.0,0.5), (1.5,-1.0,0.5),
(1.0,0.5,0.0), (2.0,-0.5,0.0), (1.5,1.0,0.5),
(2.0,0.5,0.0), (2.5,0.0,0.5).

11. 9ppd1-1pl(3)

Unit cell basis vectors Cartesian coordinates:
(1.5,-1.5,0.0), (1.5,1.5,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (1.0,0.0,0.0),
(0.5,0.5,0.0), (1.0,0.0,0.0), (1.5,-0.5,0.0),
(1.5,0.5,0.0), (1.0,-0.5,0.5);
B: (2.0,0.0,0.0), (0.5,0.0,0.5), (1.5,-1.0,0.5),
(1.0,0.5,0.0), (2.0,-0.5,0.0), (1.5,1.0,0.5),
(2.0,0.5,0.0), (2.5,0.0,0.5).

12. 1ppd2-1pl

Unit cell basis vectors Cartesian coordinates:
(1.5,-0.5,0.0), (0.5,1.5,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (0.5,0.5,0.0),
(1.0,0.0,0.0), (1.0,0.5,0.5);
B: (0.5,1.0,0.5), (1.0,1.0,0.0), (1.5,0.0,0.5),
(1.5,0.5,0.0), (1.5,1.0,0.5).

13. 2ppd3a-1pl(1)

Unit cell basis vectors Cartesian coordinates:
(3.0,-1.0,0.0), (0.5,0.5,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (0.5,0.5,0.0),
(1.0,0.0,0.0), (1.0,0.5,0.5);
B: (1.5,-0.5,0.0), (2.0,-0.5,0.5), (2.5,-0.5,0.0),
(3.0,-0.5,0.5).

14. 2ppd3a-1pl(2)

Unit cell basis vectors Cartesian coordinates:
(3.0,-1.0,0.0), (0.5,0.5,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (1.0,0.0,0.0),
(1.0,0.0,0.0), (1.5,0.0,0.5);
B: (1.5,-0.5,0.0), (2.0,-0.5,0.5), (2.5,-0.5,0.0),
(3.0,-0.5,0.5).

15. 1ppd4-1pl

Unit cell basis vectors Cartesian coordinates:
(2.0,-1.0,0.0), (0.5,0.5,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (1.0,0.0,0.0),
(1.5,0.0,0.5), (2.0,-0.5,0.5).

16. 2ppd4a-1pl(1)

Unit cell basis vectors Cartesian coordinates:
(4.0,-2.0,0.0), (0.5,0.5,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (1.0,0.0,0.0),
(1.0,0.5,0.0), (1.5,-0.5,0.0), (2.0,-0.5,0.5);
B: (2.0,-1.0,0.0), (2.5,-1.0,0.0), (3.0,-1.0,0.0),
(3.0,-1.5,0.5), (3.5,-1.5,0.0), (4.0,-1.5,0.5).

17. 2ppd4a-1pl(2)

Unit cell basis vectors Cartesian coordinates:
(4.0,-2.0,0.0), (0.5,0.5,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (1.0,0.0,0.0),
(1.0,0.5,0.0), (1.5,-0.5,0.0), (2.0,-0.5,0.5);
B: (2.0,-0.5,0.5), (2.0,-1.0,0.0), (3.0,-1.0,0.0),
(3.0,-1.5,0.5), (3.5,-1.5,0.0), (4.0,-1.5,0.5).

18. 2ppd4b-1pl

Unit cell basis vectors Cartesian coordinates:
(2.0,-1.0,0.0), (0.1,1.0,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (1.0,0.0,0.0),
(1.0,0.5,0.0), (1.5,-0.5,0.0), (2.0,-0.5,0.5);
B: (0.5,0.5,0.0), (1.0,0.5,0.5), (1.5,0.5,0.0),
(1.5,0.0,0.5), (2.0,0.0,0.0), (2.5,0.0,0.5).

19. 1ppd4-2pl

Unit cell basis vectors Cartesian coordinates:
(2.0,-1.0,0.0), (0.5,0.5,0.0), (0.0,0.0,2.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (1.0,0.0,0.0),
(1.0,0.5,0.0), (1.5,-0.5,0.0), (2.0,-0.5,0.5);
B: (0.5,0.5,0.0), (1.0,0.5,0.5), (1.5,0.5,0.0),
(1.5,0.0,0.5), (2.0,0.0,0.0), (2.5,0.0,0.5).

20. 2ppd3b-1pl

Unit cell basis vectors Cartesian coordinates:
(1.5,-0.5,0.0), (1.0,1.0,0.0), (0.0,0.0,1.0).
Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (1.0,0.0,0.0),
(1.5,0.0,0.5); (2.0,-0.5,0.5).
B: (0.5,0.5,0.0), (1.0,0.5,0.5), (1.5,0.5,0.0),
(2.0,0.5,0.5).
21. 1ppd2-2pl(1)

Unit cell basis vectors Cartesian coordinates: 
(1.5,-0.5,0.0), (0.5,1.5,0.0), (0.0,0,2.0).

Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (0.5,0.5,0.0),
(0.5,1.0,0.5), (1.0,0.0,0.0), (1.0,0.5,0.5), (1.0,1.0,0.0),
(1.5,0.0,0.5), (1.5,0.5,0.0), (0.0,0.0,1.0);
B: (1.5,1.0,0.5), (0.5,0.0,1.5), (0.5,0.5,1.0),
(0.5,1.0,1.5), (1.0,0.0,1.0), (1.0,0.5,1.5), (1.0,1.0,1.0),
(1.5,0.0,1.5), (1.5,0.5,1.0), (1.5,1.0,1.5).

22. 1ppd2-2pl(2)

Unit cell basis vectors Cartesian coordinates: 
(1.5,-0.5,0.0), (0.5,1.5,0.0), (0.0,0.0,2.0).

Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (0.5,0.5,0.0),
(0.5,1.0,0.5), (1.0,0.0,0.0), (1.0,0.5,0.5), (1.0,1.0,0.0),
(1.5,0.0,0.5), (1.5,0.5,0.0), (0.0,0.0,1.0);
B: (1.5,1.0,0.5), (0.5,0.0,1.5), (0.5,0.5,1.0),
(0.5,1.0,1.5), (1.0,0.0,1.0), (1.0,0.5,1.5), (1.0,1.0,1.0),
(1.5,0.0,1.5), (1.5,0.5,1.0), (1.5,1.0,1.5).

23. 2ppd3-3c-2pl

Unit cell basis vectors Cartesian coordinates: 
(3.5,-0.5,0.0), (0.5,0.5,0.0), (0.0,0,2.0).

Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (1.0,0.0,0.0),
(1.5,0.0,0.5), (2.0,0.0,0.5), (2.5,0.0,0.5), (3.0,0.0,0.0),
(0.0,0.0,1.0);
B: (3.5,0.0,0.5), (0.5,0.0,1.5), (1.0,0.0,1.0),
(1.5,0.0,1.5), (2.0,0.0,1.0), (2.5,0.0,1.5), (3.0,0.0,1.0),
(3.5,0.0,1.5).

24. 2cub(1), Z2

Unit cell basis vectors Cartesian coordinates: 
(1.0,0.0,0.0), (0.0,1.0,0.0), (0.0,0.0,2.0).

Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.5,0.0), (0.5,0.0,0.0),
(0.0,0.5,0.0); B: (0.0,0.0,1.0), (0.5,0.5,1.0), (0.5,0.0,1.5),
(0.0,0.5,1.5).

25. 2cub(2)

Unit cell basis vectors Cartesian coordinates: 
(1.0,0.0,0.0), (0.0,1.0,0.0), (0.0,0.0,2.0).

Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.5,0.0), (0.5,0.0,0.5),
(0.0,0.5,1.5);
B: (0.0,0.5,0.5), (0.0,0.0,1.0), (0.5,0.5,1.0),
(0.0,0.5,1.5).

26. 2cub(3)

Unit cell basis vectors Cartesian coordinates: 
(1.0,0.0,0.0), (0.0,0.5,0.0), (0.0,1.0,0.0), (0.0,0.0,2.0).

Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.5,0.0), (0.5,0.0,0.5),
(0.0,0.5,1.5);
B: (0.0,0.5,0.5), (0.0,0.0,1.0), (0.5,0.5,1.0),
(0.0,0.5,1.5).

27. 2cub(4)

Unit cell basis vectors Cartesian coordinates: 
(1.0,0.0,0.0), (0.0,0.5,0.0), (0.0,1.0,0.0), (0.0,0.0,2.0).

Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.5,0.0), (0.5,0.0,0.5),
(0.0,0.5,1.5);
B: (0.0,0.5,0.5), (0.0,0.0,1.0), (0.5,0.5,1.0),
(0.0,0.5,1.5).

28. 2cub(5)

Unit cell basis vectors Cartesian coordinates: 
(1.0,0.0,0.0), (0.0,1.0,0.0), (0.0,0.0,2.0).

Atomic Cartesian coordinates
A: (0.0,0.0,0.0), (0.5,0.0,0.5), (0.5,0.0,1.5),
(0.5,0.5,0.0); B: (0.5,0.5,0.0), (0.0,0.5,0.5), (0.5,0.5,1.0),
(0.5,0.0,1.5).

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