Size, Shape, and Compositional Effects on the Order-Disorder Phase Transitions in Au-Cu and Pt-M (M = Fe, Co, and Ni) Nanocluster Alloys

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Abstract

Au-Cu and Pt-M (M = Fe, Co, and Ni) nanocluster alloys are currently being investigated world-wide by many researchers for their interesting catalytic and nanophase properties. The low temperature behavior of the phase diagrams is not well understood for alloys with nanometer sizes and shapes. We consider two models for low temperature ordering in the phase diagrams of Au-Cu and Pt-M nanocluster alloys. These models are valid for sizes ~ 5 nm and approach bulk values for sizes ~ 20 nm. We study the phase transitions in nanoclusters with cubic, octahedral, and cuboctahedral shapes, covering the compositions of interest. These models are based on studying the melting temperatures in nanoclusters using the regular solution, mixing model for alloys. From our data, experiments on nanocubes about 5 nm in size, of stoichiometric AuCu and PtM composition, could help differentiate between the models. Dispersion data shows that for the three shapes considered, octahedra have the highest percentage of surface atoms for the same relative diameter. We summarize the effects of structural ordering on the catalytic activity and suggest a method to avoid sintering during annealing of Pt-M alloys.

Keywords: phase diagram; nanoalloy; thermodynamics; catalysis

Introduction

Complete nanoalloy phase diagrams remain an elusive holy grail of nanoscopic thermodynamics. The many variables including temperature, kinetics, size, shape, surface segregation, and structure may mean that scientists must create subsets to limit the many changes possible. This manuscript considers the low temperature, order-disorder region as relatively little is known about this important part of the diagrams. Order in alloys was considered nearly a century ago in 1919 by Tammann. He hypothesized that in alloys subjected to long anneals the atoms segregated into new ordered positions, in order to explain observed changes in resistivity [1]. In 1934, Bragg and Williams defined a long-range order parameter, S , and devised a theory for its temperature variation [2].

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Some time later, Cowley updated this model with short range and long range order parameters. He was able to determine the low temperature ordering of gold-copper alloys [3].

In simple terms, a phase diagram is a temperature and composition plot describing the relationships between two or more components. Experimentally, it can be determined by mixing the constituents at various temperatures and using structural means (x-ray diffraction, electron or neutron diffraction, etc.), to identify ordered and disordered phases. Liquidus and solidus lines require alternate methods. In principle, low temperature regions are studied by long time anneals. These are equilibrium states, and thus may be difficult to accurately ascertain, because diffusion may be limited at low temperatures. All of the Au-Cu and Pt-M phase diagrams are relatively simple, with a random fcc solid solution (A1) across the whole composition range below the melting temperatures. At lower temperatures, ordered phases (intermetallics) appear via first-order transitions to the $L1_2$ (Au_3Cu , Pt_3M , $AuCu_3$, and PtM_3) structurally ordered intermetallics and the $L1_0$ structure for the AuCu and PtM intermetallics. For platinum-nickel alloys, although low temperatures phases were known to exist, it was not until 1985 that a more accurate theoretical and experimental paper was published, describing the ordered region of the phase diagram [4]. The Pt-M phase diagrams exhibit a ferromagnetic region at lower temperatures and higher M = Fe, Co or Ni concentrations.

Modern methods of phase diagram determination include the CALPHAD (CALculation of PHase Diagram) approach. This includes software known as Thermo-Calc and PANDAT, offered by CompuTherm, LLC [5]. In the CALPHAD approach, the Gibbs energies of phases in an alloy system are described by several thermodynamic models such as the random substitutional model, the compound energy model, and the stoichiometric compound model [6]. Although the phase diagrams look simple, both (Thermo-Calc and PANDAT) require a four-sublattice model to describe the ordered and disordered regions, resulting in nontrivial programs to determine them. This has been done by the CALPHAD method for Au-Cu [7], Pt-Fe [8], Pt-Co [9], and Pt-Ni [10] phase diagrams. For the Pt-Fe phase diagram, other ordered phases appear via a second order phase transition at lower temperatures. These were considered in reference [11], but not by the CALPHAD method from which the PANDAT diagram is derived [8]. As yet, there is no general description of phase diagrams for nanoalloys, although progress is being made [12]. The general form of the shape, size, and surface segregation effects of the high temperature region of gold-copper [13, 14] and platinum-nickel [15, 16] nanophase alloys have recently been determined.

Both Au-Cu and Pt-M nanoalloys are of interest for catalytic and nanophase properties. Although bulk gold is considered the noblest among metals with a largely unreactive surface [17], it has been known for thirty years that gold in nano sizes exhibits interesting catalytic properties [18]. The explanation is that in the bulk the center of the d -band is well below the Fermi level, consequently adsorbate-metal antibonding states are filled, preventing adsorption [17]. Likewise, platinum has been of interest as a catalytic material for some time, and for about twenty years or more Pt-M and related alloys have been studied for fuel cell purposes [19]. Due principally to high cost and scarcity, it has been of interest to alloy gold and platinum with non-precious metals. Studies have shown that this also results in superior catalytic properties, especially for nano shapes and sizes, because of the high surface area and the lower coordination of surface atoms, as well as chemical effects from the alloying. Alloying has been shown to lower the d -band center of platinum, which weakens the bonding between Pt-surfaces and oxygenated species, thus raising

the oxidation reduction reaction (ORR) results [20].

One important catalytic reaction for nano gold is that of bonding with carbon monoxide [21]. This is related to low coordinated surface atom sites [22] and there may be substrate influences as well [18]. There are efforts to look at Au-Cu alloys, since copper is known to readily oxidize, compared to gold, which may improve the catalytic properties. The chemical synthesis of $\text{Au}_x\text{Cu}_{1-x}$ nanoalloys results in a solid solution throughout the composition range [23, 24], with different sizes and shapes, including nanocubes [25, 26] and nanooctahedra [26]. Recently, the effects of nanocluster structure have been investigated, and it was found that CO oxidation [27] as well as CO_2 reduction [28] was improved from ordered clusters as compared to disordered ones.

For Pt-M alloys, there is tremendous interest in high performance, cost effective ORR catalysts with suitable durability for fuel cell applications [29]. It is known that chemical synthesis of $\text{Pt}_x\text{Ni}_{1-x}$ nanoalloys can be formed throughout the composition range [30, 31], with several sizes and shapes, such as cubes [32] and octahedra [33, 34]. Octahedra are preferred, since the (111) surface has been shown to have superior ORR characteristics [35]. Likewise, $\text{Pt}_x\text{Fe}_{1-x}$ nanoalloys [36] and $\text{Pt}_x\text{Co}_{1-x}$ nanoalloys [37] can be made across the composition range with cubic and octahedral shapes [32]. An early discussion of ordering for platinum alloys and its effect on the ORR appeared in reference [38]. More recently, the case for intermetallics versus that of alloys has been considered [39, 40]. Platinum, the favored electrochemical species, is known to segregate to the surface of Pt-Ni nanoalloys [15, 16], an effect that is not considered in the models presented here. Also, iron, cobalt and nickel are smaller atoms than platinum, resulting in a more optimum Pt-Pt bond distance for the ORR reaction [38]. A linear relationship between the Pt-Pt distance and Pt-Co alloys and the ORR electrochemistry has been observed [41]. Ordering improves this effect, by spacing the atoms in a regular manner as opposed to random configurations. This further corroborates the importance of intermetallics and alloys in the search for better ORR nanochemistry.

The specific requirements for platinum based polymer electrolyte membrane fuel cells (PEMFCs) have been discussed in the literature [42]. Most cells operate around 80 C, well below the ordering transition temperatures. However, post-synthesis temperature changes of normally disordered alloys could result in undesirable structural changes that intermetallics should not have. The durability of PEMFCs is thus also improved by using intermetallics versus disordered alloys. The activity of the ORR catalysis depends on platinum and oxygenated species bonding, which in turn is related to the d -band center in platinum [20]. The ORR catalysis in platinum alloys has a d -band which has a volcano relationship, where the activity is optimal at certain compositions [20]. It has been reported that the d -band center in $\text{Pt}_n\text{Ni}_{55-n}$ nanoparticles decreases linearly with the number of Pt atoms, while that of $\text{Pt}_n\text{Fe}_{55-n}$ and $\text{Pt}_n\text{Co}_{55-n}$ are essentially flat [43]. Thus it may be possible to find an optimum d -band center in nanocluster intermetallics for the ORR catalysis.

Catalysis in Au-Cu nanoclusters has the following characteristics: gold is known to segregate to the surface [13, 14], which favorably affects the bonding of adsorbed species [28], and alloying with copper raises the center of the d -band [44], increasing the bonding of absorbed species. Thus, ordering can improve the activity, stability, and durability of the Au-Cu catalysts. We see that the intermetallics of the Pt-M and Au-Cu catalysts can offer many advantages over that of disordered alloys. The focus of this manuscript is to provide a detailed look at the low temperature regions of the Au-Cu and Pt-M phase diagrams to give scientists models for the order-disorder phase transitions in size, shape, and composition selected nanoalloys.

Methods

It is generally accepted from analysis that the melting temperatures of nanoalloys depend on the composition x , and the effective size D_e . We include in our calculations an interaction energy, Ω , similar to the bond energy in monometallic crystals. In bimetallic alloys however, the bond may exist between like or unlike elements, and should be considered as a size and composition dependent cohesive interaction [45]. Assuming that a regular solution exists [46], or that the random mixture that shows an ideal entropy of mixing, but a non-zero interchange energy, the interatomic interaction can be written as:

$$\Omega(x, \infty) = \frac{T_m(x, \infty) - xT_m(A, \infty) - (1-x)T_m(B, \infty)}{x(1-x)} \quad (1)$$

where T_m is the melting temperature, A and B represent the components in the bimetallic alloy, x denotes the molar ratio of component, A , and ∞ represents the bulk value [47]. As a function of size we have,

$$T_m(x, D_e) = xT_m(A, D_e) + (1-x)T_m(B, D_e) + x(1-x)\Omega(x, D_e). \quad (2)$$

Omega is sometimes written in terms of the bonding energy as:

$$\Omega = ZN_a[\epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2] \quad (3)$$

where Z , N_a , and ϵ denote the coordination number, Avogadro's number, and the bond energy between like and unlike atoms, respectively [48]. Since Ω depends on the bond energy which is proportional to the melting temperature, the size and compositional dependence should be similar:

$$\frac{\Omega(x, D_e)}{\Omega(x, \infty)} = \frac{T_m(x, D_e)}{T_m(x, \infty)}. \quad (4)$$

Solving $\Omega(x, D_e)$ from (4) and substituting into (2) shows that the melting temperatures of bimetallic alloys satisfy [47]:

$$\frac{T_m(x, D_e)}{T_m(x, \infty)} = \frac{xT_m(A, D_e) + (1-x)T_m(B, D_e)}{T_m(x, \infty) - \Omega(x, \infty)x(1-x)} \quad (5)$$

where $\Omega(x, \infty)$ is found from equation (1) which eventually gives

$$\frac{T_m(x, D_e)}{T_m(x, \infty)} = \frac{xT_m(A, D_e) + (1-x)T_m(B, D_e)}{xT_m(A, \infty) + (1-x)T_m(B, \infty)}. \quad (6)$$

For monometallic components A (corresponding to $x = 1$) or B (corresponding to $x = 0$) and with bond length h from Table 1 we have from Jiang's model [49]:

$$\frac{T_m(D_e)}{T_m(\infty)} \approx \exp \left[-\frac{2\lambda S_{vib}(\infty)}{3R \left[\frac{D_e}{6h} - 1 \right]} \right] \quad (7)$$

where R is the universal gas constant and λ is a shape factor from Table 2. The vibrational melting energy is given by

$$S_{vib}(\infty) = S_m(\infty) - S_{pos}(\infty) - S_{el}(\infty) \quad (8)$$

	h (nm) [54]	$T_m(\infty)$ (K) [54]	$S_m(\infty)$ (J/mol-K) [54]	$S_{pos}(\infty)$ (J/mol-K) see eq.(9)	ρ_s (gm/cm ³) [54]	ρ_l (gm/cm ³) [54]	M (kg/mol) [54]	σ_{sl} (N/m) [55]	θ_D @298K [56]
Au	0.288	1337	9.386	2.768	19.30	17.30	0.19657	1.145	178K
Cu	0.256	1358	9.768	2.831	8.96	8.00	0.06355	1.330	310K
Pt	0.278	2041	10.862	2.306	21.40	19.70	0.19508	1.748	225K
Fe	0.248	1811	7.623	2.826	7.86	7.02	0.05585	1.860	373K
Co	0.250	1768	9.163	3.340	8.90	7.67	0.05893	1.883	386K
Ni	0.249	1728	10.114	2.902	8.90	7.91	0.05869	1.796	345K

Table 1: Values of bulk parameters

where m refers to melting, pos is positional and el is electronic. $S_{el}(\infty) \approx 0$ for metallic crystals [50]. For monometallic crystals we have

$$S_{pos}(\infty) \approx -R(x_A \ln x_A + x_V \ln x_V) \quad (9)$$

where x_A and $x_V = 1 - x_A$ are the mole fractions of the crystals and vacancies, respectively [51]. For a melting process [51]:

$$x_A = V_s/V_l = \rho_l/\rho_s \quad (10)$$

where V is the molar volume, ρ refers to density, and s and l refer to solid and liquid, respectively. For model 2 [52], equation (7) is replaced by:

$$\frac{T_m(D_e)}{T_m(\infty)} \approx 1 - \frac{\alpha_{shape}}{D_e} \quad (11)$$

where the α_{shape} parameter depends on the shape, elements, and thermodynamic properties of the nanocluster, and is listed in Table 2. A third possible model may be based on reference [53], which replaces (7) by

$$\frac{T_m(D_e)}{T_m(\infty)} \approx 1 - \frac{10^9(\varepsilon + 4)\sigma_{sl}M}{H_m(\infty)\rho_s D_e} \quad (12)$$

where ∞ refers to bulk values $H_m(\infty) = T_m(\infty)S_m(\infty)$ is the molar enthalpy at melting temperature, M is the molar mass, ρ_s the density in solid phase, and σ_{sl} the interface tension between solid and liquid. This model produces a ratio for equation (12) of about zero around $D_e \sim 7$ nm, and appears not as accurate as the other two models, so it will not be considered further. Equations (7), (11) and (12) apply to the components A and B of the alloy system and D_e is in nanometers.

Now the ordering temperatures are related to the melting of Au-Cu and Pt-Fe alloys where the ordering is given by relation to the Debye temperature θ_D [59, 60]:

$$\frac{T_o(x, D_e)}{T_o(x, \infty)} \approx \frac{\theta_D(x, D_e)}{\theta_D(x, \infty)}. \quad (13)$$

Shape	λ [57]	α_{shape}^{Au} (nm) [58]	α_{shape}^{Cu} (nm) [58]	α_{shape}^{Pt} (nm) [58]	α_{shape}^{Fe} (nm) [58]	α_{shape}^{Co} (nm) [58]	α_{shape}^{Ni} (nm) [58]
Cube	1.00	2.43	2.78	2.14	1.77	2.53	1.59
Octahedron	1.22475	0.92	2.56	1.31	4.10	3.09	0.79
Cuboctahedron	0.66921	1.22	1.84	1.02	1.78	1.69	0.70
Sphere	1.00	1.81	1.69	1.50	2.55	2.53	1.64

Table 2: Values of shape parameters for Models 1 and 2

Combining the Lindemann analysis of melting with the Debye temperature, we have

$$\theta_D(\infty) = c[T_m(\infty)/(MV^{2/3})]^{1/2}, \quad (14)$$

where c , M and V , are a constant, the atomic or molecular weight, and the molar volume, respectively [61]. Since this relationship has been used for Au-Cu and Pt-Fe alloys and the ordering transition is related for Pt-Co and Pt-Ni alloys we have:

$$\frac{\theta_D(x, D_e)}{\theta_D(x, \infty)} \approx \left[\frac{T_m(x, D_e)}{T_m(x, \infty)} \right]^{1/2}. \quad (15)$$

Finally, the ordering temperature as a function of diameter and composition is [47, 49, 59]:

$$\frac{T_o(x, D_e)}{T_o(x, \infty)} \approx \frac{\theta_D(x, D_e)}{\theta_D(x, \infty)} \approx \left[\frac{T_m(x, D_e)}{T_m(x, \infty)} \right]^{1/2}, \quad (16)$$

where $T_m(x, D_e)/T_m(x, \infty)$ is found from equation (6). These equations are valid for all sizes for model 1, as it depends on the Debye temperature, and is valid for $T < \theta_D/2$ which is about $T \approx 100$ K for the alloys we consider at $T = 298$ K, see Table 1 [62, 63]. It is known that the Debye temperature falls with increasing temperature [64], so that for our purposes, model 1 should be valid at all sizes. Model 2 is valid for $D_e \sim 4 - 5$ nm and larger, as the thermodynamic considerations need to be revised for smaller dimensions [52], i.e. we do not correct for corner and edge atom effects, which become important for clusters below 4 nm in diameter.

Results and Discussion

There exist previous models of ordering in nanoalloys. Technically the ordering temperature is related to the melting temperature via equation (16), but not all melting models discuss this relationship. Of the two models presented, only model one, reference [49], discusses the ordering transition. In addition to this reference, Li [65] generalized the Bragg-Williams model to include size and shape effects by considering edge and corner atoms, making the model valid for small (~ 1 nm) dimensions, even though it is not certain that such small particles are ordered. Also,

Delogu [66] considered the order transition in nanoparticles, and showed that the ordering temperature varies linearly with the reciprocal of the particle radius. More recently, Yang [67] looked at the size and dimensionality of the ordering transition. Theoretical models, such as molecular dynamics (MD) and density functional theory (DFT) have also been considered for Au-Cu and Pt-Ni alloys and intermetallics. These methods are limited to smaller size dimensions due to the large atom configurations necessary for such methods. Delogu considered ordering in 2 to 20 nm AuCu₃ nanoparticles using MD simulations and found that gold surface segregation takes place, the ordering temperature is dependent on kinetics, and the transition temperature decreases with decreasing particle size [68]. Goh used an empirical atomistic potential for AuCu clusters up to 4 nm, but found that due to gold surface segregation, ordered phases were not favorable [69]. For Pt-Ni nanoparticles, Wang used embedded atom potentials and the Monte Carlo (MC) method for particles between 2.5 to 5 nm in diameter [70]. They found an order transition in 4 to 5 nm particles at 600K, but note that this was not a thorough study. Cheng used MC and MD methods for 561 and 923 Pt-Ni atom cuboctahedral clusters, and found a short-range order parameter in the clusters had an L1₀ transition temperature from 1600 to 1700K [71]. Also, a Monte Carlo simulation of PtFe nanoclusters up to 8.5 nm in size determined phase behavior and dependence of ordering temperature on particle size [72]. A similar study on PtFe cuboctahedra of sizes up to 5 nm was conducted by Yang et al in 2006 [73].

We elect to consider a phenomenological approach as it is not clear that ordered phases exist in clusters smaller than ~ 2 -3 nm, and it is also possible to study the whole composition range with sizes up to 20 nm. In Figure 1, we show the PANDAT derived phase diagrams of Au-Cu and Pt-M alloys. In Figures 1A and 1B-D, the green circles represent the AuCu₃ and PtM₃ regions of stability, the red circles the AuCu and PtM regions, and the yellow circles the Au₃Cu and Pt₃M regions. The lower circles are the ordering temperatures, and the higher circles are the melting transitions, both of which we use in our analysis. Although we use the liquidus lines, it is evident that for much of the phase diagrams, the liquidus and solidus lines are very close, so that the final choice would only result in a few percentage points relative temperature difference no matter which one was chosen.

Although these phase diagrams represent bulk behavior, there is evidence that some nano non-stoichiometry exists as well. Recently, Mendoza-Cruz investigated the Au-Cu ordering transition in nanocubes and found that the composition ranged from $0.22 < x(\text{Au}) < 0.35$ for AuCu₃, from $0.5 < x(\text{Au}) < 0.65$ for AuCu and from $0.75 < x(\text{Au}) < 0.88$ for Au₃Cu [60]. In addition, for PtNi, Leonard found a region of composition stability of $0.39 < x(\text{Pt}) < 0.54$ [74]. We conclude that the composition dependence of the nanosized ordering transition is not stoichiometric, but has a range where it occurs.

The L1₂ and L1₀ intermetallic structures are shown in Figure 2. The L1₂ phase is a cubic structure, *Pm3m*, (Wyckoff notation) with either Au(Pt) or Cu(M) rich constituents. The L1₀ phase is tetragonal, *P4/mmm*, with alternating layers of Au(Pt) and Cu(M). In the case of the magnetic nanoalloys PtFe and PtCo, this is the preferred phase, as the tetragonal structure allows for easy and hard coercivity axes depending on the alignment of the crystal structure. Both phases transition to the A1 phase, *Fm3m*, which is also cubic, with random elements in positions of the cubic geometry. It is possible to define long range order (LRO) parameters based on sublattices of the L1₀ phase and the L1₂ phase [75]. These parameters take the value $P_{LRO} = \pm 1$ in the perfect bulk phases

A.

B.

C.

D.

Figure 1: PANDAT phase diagrams for Au-Cu, Pt-Fe, Pt-Co, and Pt-Ni

Figure 2: L1₀ and L1₂ structures

and $P_{LRO} = 0$ in the disordered A1 phase.

The ordering temperature as a function of composition, x , and effective size, D_e , for the two models and three shapes is shown in Figure 3 for Au-Cu, Figure 4 for Pt-Fe, Figure 5 for Pt-Co, and Figure 6 for Pt-Ni. The surface representing the ordering temperature computed by model 1 has an RGB color stronger in the RG component (yellow-to-green) and the color of the surface representing model 2 has a stronger B component (blue). The figures illustrate clearly that in general the model 1 ordering temperature is higher than the corresponding model 2 temperature with a clear exception for the cuboctahedral Pt-Co and Pt-Ni clusters. In each figure we also added a representation of two clusters: one at the bottom for low temperature (L1₂ and L1₀ phase) and one for at the top for high temperature (A1 phase). Atoms are represented by spheres with a suggestive color. We use the color gold for Au, copper for Cu, silver for Pt, red (rust) for Fe, cobalt blue for Co, and green for Ni. The ordering compositions are found from the selected red, green, and yellow data in Figures 1A, 1B, 1C, and 1D, and the size range is from 4 to 20 nm.

It is evident from Figures 3 - 6 that the largest separation between the models occurs in cubes for both the AuCu and PtM compositions. Furthermore, the gap widens as the cluster size becomes smaller. In Figure 7, we show the AuCu and PtM phase diagrams at $D_e = 5$ nm. For AuCu both models predict the A1 phase above 400 C, while for PtM the highest transition for model 1 versus model 2 varies from 100 C to 50 C to 30 C Fe, Co, and Ni, respectively. The models are well separated in terms of predicted ordering temperature, and the cube at 5 nm and stoichiometric composition, is the optimum size and shape for determining which model is most accurate. At other compositions and sizes, the models may coincide, and both models approach the bulk value near $D_e = 20$ nm and higher.

We compare the various models with experimental data in Figure 8. Figures 8A-C are from reference [60], where the authors conducted electron microscopy work on Au-Cu nanocubes across the composition range. These nanocubes were annealed post-synthesis in a vacuum chamber under high vacuum (5×10^{-5} Torr) for two hours at selected temperatures. We select the models for composition ranges of the cubic geometry and plot the experimental data (ordered and disordered) in the figures. The ordered and disordered data have error bars (approximate) to represent the

Figure 3: Ordering temperature as a function of composition, x , and effective size, D_e , for the two models and three shapes for Au-Cu alloys

Figure 4: Ordering temperature as a function of composition, x , and effective size, D_e , for the two models and three shapes for Pt-Fe alloys

Figure 5: Ordering temperature as a function of composition, x , and effective size, D_e , for the two models and three shapes for Pt-Co alloys

Figure 6: Ordering temperature as a function of composition, x , and effective size, D_e , for the two models and three shapes for Pt-Ni alloys

experimental variation. For the most part, these cubes are too large to determine which model is most accurate. Figures 8D and 8E are from references [28] and [27], respectively. The authors annealed spherical AuCu nanoparticles 7 and 8 nm in diameter, which we model with spherical geometry. In both cases, the annealing temperatures were low enough to produce intermetallics, but no anneal took place at higher temperatures to produce the A1 phase. Also, Figures 8G and 8H are from reference [76]. The authors annealed ~ 3 nm AuCu and AuCu₃ nanoparticles in a reducing atmosphere at 250 C and 300 C. This is at the lower range of our analysis and below the size range of reference [69] where the authors did not find an order-disorder transition.

In Figure 8I we show PtFe spherical nanoparticles of about 6-7 nm in size annealed at 700 C [77], well below the predicted transition temperatures of 1200 C. This resulted in ordered PtFe nanoparticles. In comparison PtFe spheres, about 4 nm in size are shown in Figure 8J. These were annealed at 800 C, 900 C and 1000 C, with the lower temperature anneals resulting in partially ordered particles [78]. In Figure 8K we show 6 nm Pt₃Co spherical particles annealed at 400 C and 700 C [79]. The modeling predicts that the 700 C anneal should have resulted in the A1 disordered phase, but the data produces ordered nanoparticles. The authors [79] state a ± 1 nm deviation in particle size, and also that there was a platinum shell at the surface, which may have affected the stoichiometry, thus the modeling. In Figure 8L, from reference [80], the authors annealed spherical PtNi particles, about 8 nm in diameter, at 550 and 600 C, which we again model with the spherical parameters. Models 1 and 2 correctly predict the ordered L1₀ phase.

An analysis of the models and the available experimental data indicates that a definitive case cannot be made between the models as not enough annealing experiments have been done between the ordered and disordered phases. We note that with the exception of reference [60], these experiments have not been designed to look at the order-disorder transition, but rather to produce ordered phases, primarily to determine the resulting catalytic behavior.

Both of the 3D models in Figures 3-6 can be projected on the D_e axis for a 2D plot of the ordering temperature vs D_e , if the composition is known. In Figure 9, we make such plots. Other compositions and phase diagrams may be considered in these 2D plots of $T_o(C)$ vs D_e , and is shown in Figures 9A-D. We choose to present the ordering temperature of model 2 versus D_e for the three stoichiometric compositions and three shapes considered. Figure 9A shows that for the Au-Cu stoichiometric intermetallics, the ordering temperature follows that of the bulk phase diagram, i.e. AuCu has the highest ordering temperature, then AuCu₃, and last Au₃Cu. For the shapes considered, the cuboctahedra have the highest ordering temperature, then octahedra, followed by cubes. This same shape sequence was found by Li [65]. For Pt-M, the trends are similar, i.e. the data follows the trends in the bulk phase diagrams, and the data is shown in Figure 9B-D.

The most interesting property of Au-Cu and Pt-M nanoclusters is for catalytic applications. In the case of Pt-Ni nanoclusters, it is known that octahedra provide the best shape for these applications, due to the (111) surface orientation [35]. In Figure 10, we show the dispersion relationships for the three shapes considered versus d_{rel} . Here d_{rel} is defined as

$$d_{rel} = \frac{d_{sph}}{d_{at}} = d_{at}^{-1} \left(\frac{6}{\pi} N_T \frac{V_u}{n_u} \right)^{1/3}, \quad (17)$$

so that d_{rel} is defined as the ratio of the diameter of a sphere with a volume equal to N_T times

A.

B.

C.

D.

Figure 7: AuCu, PtFe, PtCo, and PtNi phase diagrams at $D_e = 5 \text{ nm}$

Figure 8: Comparison of the two models with experimental data

Catalyst	MA_O/MA_D	Shape	Size (nm)	Reference
AuCu	3.4	Sphere	7	[28]
PtFe	2.13	Sphere	6.5	[77]
PtNi	1.27	Sphere	7.5	[80]
Pt ₃ Co	3.25	Sphere	7	[79]

Table 3: Electrochemical ordering parameters and effects

the volume occupied by an atom in the unit cell, where V_u =volume of the unit cell, n_u =number of atoms in the unit cell [81]. It is known that d_{rel} depends only on the crystal structure and total number of atoms, N_T , so that $d_{rel} = 1.1055 \times N_T^{1/3}$ for fcc structures, of any composition [81]. In Figure 10, we show $FE = N_S/N_T$, the dispersion for the three shapes, and N_S is the number of surface atoms. FE can be modeled with a power law as d_{rel} increases. From the exponents of the power laws, we see that for equivalent sizes, octahedra have the highest percentage of surface atoms, followed by cubes, then cuboctahedra. This may provide an additional reason why octahedra are preferred for catalytic applications, as well as the (111) surface orientation.

In Table 3, we show the measured effects of ordering in terms of the mass activity of the electrocatalytic cells of ordered nanoalloys versus disordered alloys, MA_O/MA_D , and include the shape and size effects. In all cases, ordering improves the mass activity, with up to 3.4 times that of disordered alloys in some studies. Table 3 shows that all these studies have spherically shaped nanoalloys. Common chemical methods of creating nanoclusters result in the random A1 phase at low temperatures and high temperature anneals are required to form ordered phases. We are aware of at least one reference [82], which created ordered PtFe octahedra at room temperature from sputtering, a non-equilibrium process. These clusters were analyzed for their magnetic properties, and the catalytic properties are unknown. We mention that Table 3 represents a cross section of a variety of results, with some data left out due to a lack of comparison with ORR data on A1 phase material or other considerations.

For the Pt-M alloys, the high temperature anneals often create a problem of sintering in nanoparticles. This problem has been addressed in a recent reference [77]. The authors created a thin (a few monolayers) of a carbon coating around the PtFe nanoparticles that effectively protected them from agglomeration during annealing. Moreover, the particles retained the catalytic improvements of annealing, as Table 3 indicates, with a factor of 2 improvement over the un-annealed particles. We are not aware of this technique being transferred to Pt-Co or Pt-Ni nanoalloys.

High-temperature anneals may also cause nanocluster alloys to assume the lowest energy state with a spherical geometry, although as we have already discussed, low temperature anneals of ~ 300 C in Au-Cu alloys allowed them to retain the cubic shape [60]. In the case where the spherical shape is taken, we note that for model 1, the shape factors of the cube and the sphere are the same, see Table 2. Therefore, the phase diagrams and the order-disorder transitions for model 1 should be similar for the cubic and spherical geometry.

A.

B.

C.

D.

Figure 9: Ordering temperatures vs D_e for different shapes

Figure 10: Dispersion vs d_{rel} for the three different shapes considered

Conclusions

We have derived the size, shape, and composition dependence of the intermetallics in the Au-Cu and Pt-M phase diagrams. The ordering temperature is close to the bulk value as $D_e \sim 20$ nm for most of the alloys considered, with only a gradual rise from 20 to 50 nm. We find that the ordering temperature in nanoclusters follows the trends in the bulk, and that of the shapes considered the cuboctahedron has the highest ordering temperature, followed by the octahedron and the cube. In the case of the dispersion of the three shapes, it is found that octahedra have the highest concentration of surface atoms for the same relative diameter of the clusters. We have summarized the results of structural ordering on the catalytic properties. Also, we suggest the method used to solve the problem of sintering in PtFe nanoparticles be attempted for Pt-Co and Pt-Ni nanoalloys. These phase diagram trends can in principle be extended to other alloy systems. The Au-Cu and Pt-M systems were chosen because of their similar phase diagrams and importance for catalytic activity.

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