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COMPETING MECHANISMS FOR ORDERING TENDENCIES IN BCC $CuAuZn_2$ AND FCC AuFe ALLOYS

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INTRODUCTION

We have implemented a first-principles theory of short-range order in high-temperature, disordered, multicomponent alloys (and magnetic and paramagnetic binary alloys) which determines the atomic (and magnetic) pair-correlations from the underlying local-density-functional electronic structure of the chemically (homogeneously) random alloy. Features in diffuse scattering intensities may be directly related to their electronic origins, for a microscopic, system-dependent understanding of the ordering tendencies, or atomic short–range order (ASRO). We discuss briefly the electronic origins, and the novel competitions they produce, for the ordering tendencies in two different alloy systems. First, we discuss the ASRO indicating a high–temperature B2–type state in BCC (Heusler) $CuAuZn_2$; the ordering tendency is determined by a competition between the different types of order associated with each of the three independent pair–correlations, with the dominant ordering originating from band filling. Second, the controversial $< 1, \frac{1}{2}, 0 >$ ASRO observed in FCC AuFe alloys (prepared at high–temperature and rapidly quenched) arises from a competition between ordering (from hybridization) and clustering (from band–filling) tendencies within the same pair-correlation.

We investigate the stability of the disordered solid solution phase of metallic N-component alloys by calculating the atomic (and/or magnetic) pair–correlation function(s) using a (mean-field) thermodynamic, linear-response approach based on a first-principles description of the finite-temperature, electronic grand potential of the disordered alloy[1–5]. The infinite–temperature limit (i.e., $T \rightarrow \infty$) of the theory (*i.e.*,

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no ASRO) is the homogeneously random state and is our linear–response reference state; hence the use of Korringa-Kohn-Rostoker Coherent-Potential-Approximation[2,3,6] (KKR-CPA) electronic-structure formalism. Because of its electronic–structure basis, a strength of the approach is that peaks in the alloy's pair–correlation functions (or Warren-Cowley parameters) may be directly related to specific electronic features. Such information is particularly valuable when the ASRO is a precursor of the low–T ordered state, as is the case for $CuAuZn_2$, e.g., since it may reveal much about the electronic origin of the long-range ordered state. From a practical standpoint, knowledge of the high-T behavior is relevant to most materials processing. Furthermore, it is the case that pair–correlations in the perhaps more technologically interesting N-component alloys may be calculated with little more effort than for binaries. The various applications, details, and improvements to this first–principles, concentration–wave approach may be found in refs.[1–5,7,8].

CONCENTRATION FLUCTUATIONS AND ASRO IN MULTICOMPONENT ALLOYS

For any N-component alloy, i.e., $A_{c_A}B_{c_B}...N_{c_N}$, any chemical configuration (whether ordered or disordered) can be described by a set of site–occupation variables $\xi_{\alpha,i}$. Here $\xi_{\alpha,i}$ is 1(0) if an α-type atom does (does not) occupy the ith site in the lattice. The thermodynamic average of $\xi_{\alpha,i}$, $<\xi_{\alpha,i}>$, is then the average concentration (or probability) of an α atom at that site, $c_{\alpha,i}$. At very high temperatures the alloy is (assumed to be) homogeneously disordered and $c_{\alpha,i} = c_\alpha$ for all sites i. The KKR-CPA electronic structure and energetics are then an appropriate basis for describing the configurational average over the electronic degrees of freedom for this reference state[1,3–5]. Furthermore, the *inhomogeneous* version of the KKR-CPA theory provides a formal expression for the electronic grand potential for any atomic arrangement, denoted by $\Omega_e(T, \mu, \{\xi_\alpha^i\})$, which can be used to study the properties of the chemical fluctuations and hence the ASRO. By applying small, inhomogeneous 'external' chemical potentials $\{\delta\nu_{\alpha,i}\}$ to induce changes in the site-occupational probabilities, $\{\delta c_{\alpha,i}\}$, we consider the linear response of the homogeneously disordered alloy. The compositional correlations can then be investigated via the fluctuation-dissipation theorem which connects these responses to the Warren–Cowley parameters, $\alpha_{ij}^{\alpha\beta} = \delta c_{\alpha,i}/\delta\nu_{\beta,j} = \beta(\langle\xi_{\alpha,i}\xi_{\beta,j}\rangle - \langle\xi_{\alpha,i}\rangle\langle\xi_{\beta,j}\rangle)$, where $\beta = (k_B T)^{-1}$.

It is important to note that the site probabilities (occupation variables) satisfy a constraint $\sum_\alpha c_\alpha^i = 1$ ($\sum_\alpha \xi_\alpha^i = 1$) on every site i. It is obvious then that one of the concentration variables may be eliminated by the constraint so as to only work with the independent chemical degrees of freedom. Effectively, the N–dimensional concentration space then can be fully described by a (N-1)–dimensional reduced ("host") space.

The experimentally–measured diffuse intensities can be expressed as linear combinations of the Warren–Cowley parameters $\alpha(\vec{k})$ which are related to the correlation function via

$$\alpha_{\alpha\beta}(\vec{k}) = \frac{q_{\alpha\beta}(\vec{k})}{\bar{c}_\beta\,(\delta_{\beta\alpha} - \bar{c}_\alpha)} \quad . \tag{1}$$

Experimentally *any* $N(N-1)/2$ independent SRO parameters can be determined by making as many measurements, say by varying the energies in an anomalous x-ray experiments. Traditionally, the off–diagonal elements of the Warren–Cowley matrix

have been reported. The central result of the present first–principles theory for the pair–correlation function is

$$\left[q^{-1}\left(\vec{k},T\right)\right]_{\alpha\beta} = \left[\delta_{\alpha\beta}\frac{1}{\bar{c}_\alpha} + \frac{1}{\bar{c}_N}\right] - \beta\left[S^{(2)}_{\alpha\beta}(\vec{k},T) - \Sigma_{\alpha\beta}(T)\right] \quad . \tag{2}$$

Here $S^{(2)}_{\alpha\beta}(\vec{k})$ is the Orstein-Zernike direct-correlation function evaluated about the *homogeneous* state. It is defined in real–space as $S^{\alpha\beta}_{ij} = -\left(\frac{\partial^2\langle\Omega_e\rangle_0}{\partial c^i_\alpha \partial c^j_\beta}\right)$, and it is the chemical stability matrix of the disordered alloy. The temperature–dependent $\Sigma_{\alpha\beta}$ is the so-called Onsager cavity field and, for this mean–field theory, maintains the diagonal part of the fluctuation-dissipation theorem, i.e., $q^{ii}_{\alpha\beta} = \bar{c}_\alpha\left(\delta_{\beta\alpha} - \bar{c}_\beta\right)$, or $\alpha_{\mu\nu}(\vec{R} = (0,0,0)) = 1$[4,11,12]; it is the most important for long–ranged interactions[4,11]. Eq. (2) is the N-component generalization of the first-principles, concentration-wave formalism developed initially by Györffy and Stocks[1] and further by Staunton, Johnson, and Pinski[4] who elucidated the details and importance of charge–transfer effects and Onsager corrections. Details on the multicomponent version have been discussed in two recent papers on the ASRO in the FCC Cu–Ni–Zn alloys[7,8].

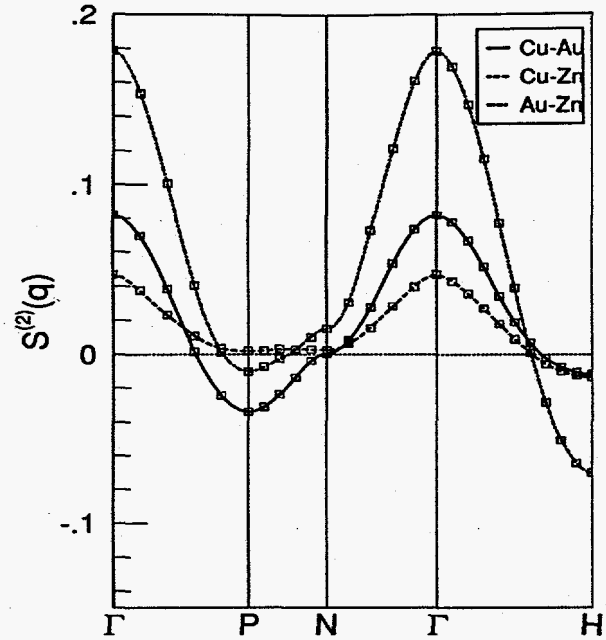
Within linear-response theory, $[q^{-1}]_{\alpha\beta}$ is proportional to the Hessian of the free energy, and most of the analysis of concentration waves in N-component alloys is related (in a somewhat complicated way[9,10]) to the eigenvectors and eigenvalues of this matrix, as is the definition of the spinodal temperature[10]. Notice that $S^{(2)}_{\alpha\beta}$ is a $(N-1)\times(N-1)$ matrix and can be roughly viewed as a *effective chemical pair–interaction* in this "host" picture. Thus, our mean–field theory permits a straightforward interpretation of the correlation function in terms of pairwise interactions (in real space, if so desired) – analogous to that of Gorsky–Bragg–Williams[13,14] but it is more robust owing to the electronic basis and concentration dependence of the theory[4,5].

SELECTED RESULTS IN A FCC AuFe BINARY AND BCC $CuAuZn_2$ TERNARY

For the ternary alloys to be discussed here, we have used the band–energy–only approximation (i.e., only band–filling effects were kept, no electrostatic and exhange–correlation (magnetic) effects), whereas, for AuFe[19], all terms were kept[4]. This approximation typically captures the main physics but overestimates the spinodal temperature, T_{sp}. The first–principles, Disordered Local Moment (DLM) model[3] was used to model the paramagnetic state of AuFe. In the ASRO calculations, potentials were obtained self-consistently from the scalar–relativistic KKR-CPA, using local-density-functional theory. Also, we imposed the constraint of a fixed Bravais lattice.

BCC $CuAuZn_2$ Heusler Alloy

In Fig. 1, we show the calculated $S^{(2)}_{CuZn}$, $S^{(2)}_{CuAu}$, and $S^{(2)}_{AuZn}$ for BCC $CuAuZn_2$ along the main symmetry directions in the BCC reciprocal lattice. The minimum of $S^{(2)}_{\mu\nu}$ results in a maximum in the corresponding $\alpha_{\mu\nu}(\vec{k})$, see eq. (2). The absolute maximum (dictated by $S^{(2)}_{AuZn}$) clearly falls at the (100) H-points, indicating a partially–ordered B2 (CsCl–type) ordering tendency, as is indeed observed[16,17].



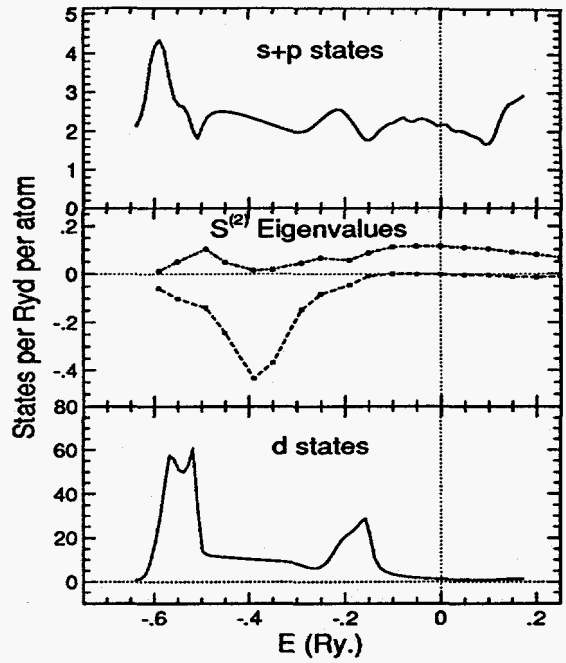


Figure 1. $CuAuZn_2$ $S^{(2)}$ pairs (in Ryd) along BCC Brillouin zone symmetry lines.

Figure 2. The two $< 1,0,0 >$ eigenvalues (in Ry) of $CuAuZn_2$ $S^{(2)}$ (middle) and L-decomposed DOS (top [bottom] s+p [d] states) versus energy (Ry). The vertical line is the Fermi level.

Interestingly, ternary $CuAuZn_2$ is a rather ideal case where its ordering properties are dictated completely by the behavior of the endpoint BCC binaries. The Cu-Zn pair clearly indicates a propensity for weak B2–type order, with no negative minimum (energetically favorable fluctuations) elsewhere, as observed in BCC CuZn[18]. At high temperatures, the Cu-Au pair shows a stronger propensity for B32–type order (i.e. $\vec{k} =< \frac{1}{2}, \frac{1}{2}, \frac{1}{2} >$, the P-point), as, in fact, we find for the binary CuAu alloy on a fixed BCC lattice. The Au-Zn pair, with its strong $< 1,0,0 >$ ordering tendency, also has a weak minimum at the P-point indicating a low-T propensity for a Heusler structure (formed by a $< 1,0,0 > + < \frac{1}{2}, \frac{1}{2}, \frac{1}{2} >$ ordering wave). With no positive contributions at the P-points (i.e. no energetically unfavorable dissent from the other pairs), $S^{(2)}$ supports a low-T Heusler phase, as is observed[18].

For $CuAuZn_2$, the electronic origins for this strong partially–ordered B2 (and subsequent Heusler) phase formation is rather straightforward. Fig. 2 shows the density of states (DOS) for the disordered alloy, along with the two (N-1, N=3, a ternary) $< 1,0,0 >$ eigenvalues of $S^{(2)}$ plotted versus energy. This was obtained by fictitiously moving the Fermi energy, in a rigid-band fashion, from the true Fermi level. The second eigenvalue is obviously not associated with $< 1,0,0 >$–type ordering because of its negative value at $< 1,0,0 >$; it, in fact, promotes clustering. This eigenvalue is nearly zero at the Fermi level, but is increases in significance when the energy is reduced to make d-band filling important. Roughly speaking (and a full analysis has yet to be completed), an almost half–filled s–p band is mostly responsible for maximum (positive) $< 1,0,0 >$ eigenvalue at the Fermi level. This eigenvalue governs the high–T behavior and, thus, the resulting B2–type ordering. The analysis is complicated because the eigenvalue in question is a function of the three independent pairs, each perhaps depending on

different electronic effects. Because the eigenvalue of the $S^{(2)}$ dictates the temperature scale, the plot indicates that little increase in T_{sp} would be found if, through alloying, the Fermi level was altered. Of course, it is possible that alloying with some other element may significantly alter the electronic structure and allow for an increase in T_{sp} (a non–rigid–band effect). By understanding the role of the various electronic mechanisms responsible for the $\vec{k}$–dependent behavior of each of the independent pair–correlations, it should be possible to "design" a partially–ordered B2 state with a higher T_{sp} by, *e.g.*, emphasizing one pair at the H–point while de–emphasizing another at at the P–point, by, for instance, a further alloying addition. Such effects bear exploration for more technological important alloys, such as $NbAlTi_2$.

We note the above somewhat limited interpretation of ASRO in this Heusler alloy did not require the determination of the site–probability distributions, which is needed for a full description of the ASRO, or the partially–ordered state that is suggested by it. This complication requires a discussion beyond the scope of this paper, see ref.[10]. To determine uniquely the ASRO in N-component alloys more than just a wavevector is required. In contrast to a binary alloy, where the wavevector (due to the Ising symmetry: if not A, then B) determines uniquely the type of ordered state in stoichiometric alloys, concentration waves in in an ABC_2 alloy, for instance, may have numerous partially–ordered stoichiometric phases delineated only by the polarization: one can have, e.g., C ordering against half A and half B. These polarizations (the analog of normal modes in a phonon calculation) are related to the eigenvectors of $[q^{-1}]_{\alpha\beta}$ and, hence, are determined by the electronic interactions in the system[8,10]. It follows[10] that the data from diffuse-scattering experiments also provide this polarization information to determine the ASRO uniquely.

$< 1, \frac{1}{2}, 0 >$ ASRO IN <u>Au</u>Fe ALLOYS

The DLM paramagnetic state corresponds to an alloy which is prepared and then rapidly quenched from high temperature, as done in the experiments which observe the $< 1, \frac{1}{2}, 0 >$ ASRO, see ref.[19]. With this in mind, we find[19] that the novel $< 1, \frac{1}{2}, 0 >$ ASRO in paramagnetic <u>Au</u>Fe alloys has a similar origin to the ASRO found in FCC $Ni_{50}Pt_{50}$. Recall that contrary to standard tight-binding arguments, NiPt orders with $< 1, 0, 0 >$– (or $L1_0$–) type order even though the d–bands are very nearly filled[15]. However, as first noted for NiPt[15], there is an *electronic size* effect at play which results from a large d-bandwidth mismatch, and which competes with the band–filling effects. Owing to the disparity between the d-bandwidths of the elemental metals, low-lying, t_{2g}-type bonding d-states are created through alloy hybridization and then occupied at the expense of the antibonding states. These t_{2g} d-states, whose lobes point towards the FCC near-neighbors, promote $L1_0$–type order[15]. So, in NiPt, despite the alloy's d-states being nearly filled, this mechanism produces $L1_0$–type ASRO, a precursor to the observed low-T $L1_0$ phase.

Compared to NiPt, the ordering tendency in paramagnetic <u>*Au*</u>*Fe* alloys is somewhat complicated by the 'local exchange splitting' in the electronic structure associated with the Fe local moments, as shown in Fig. 3 by the double-peak in the Fe-associated DOS[19]. Fig. 3 also shows that the filled Au d-states hybridize strongly at low energies with about half of the local-exchange-split Fe states. This causes the occupation of the low-lying, t_{2g} states, as in NiPt, and promotes $< 1, 0, 0 >$–type order. To conserve electrons, the high–energy, exchange-split, Fe states must become partially filled. In filling those antibonding states near the Fermi level, a clustering effect is promoted. It

is a competition between $< 1,0,0 >$ ordering and clustering that is responsible for the $< 1,\frac{1}{2},0 >$ special–point order in AuFe, including the ferromagnetic correlations found in the paramagnetic susceptibility[19]. This can be seen by studying the band–filling effects in $\alpha(\vec{k})$, as done for the ternary above. Raising the Fermi level by as much as 50 mRy does not shift the $< 1,\frac{1}{2},0 >$ peak, whereas lowering it by 50 mRy produces roughly equal intensity maxima at all $< 1,0,0 >$ and $< 1,\frac{1}{2},0 >$. With a reduction of 100 mRy, robust $< 1,0,0 >$ ordering is achieved because the Fermi level is now located at the trough of the Fe double-peak, see Fig. 3, and the antibonding states have been depopulated.

We find, due to the same mechanism described above, that ferromagnetic AuFe would show only $< 1,0,0 >$ ASRO, suggesting that such long–range order may be created via magnetic annealing[19]. Finally, a similar explanation holds for the $< 1,\frac{1}{2},0 >$ magnetic SRO seen in CuMn alloys, see refs.[20,21].

SUMMARY AND FUTURE

We have briefly discussed the ASRO in AuFe and $CuAuZn_2$. The general points to carry away are that (1) we have implemented a first-principles theory of ASRO in N-component alloys which allows determination of the electronic origins of said ASRO; (2) such calculations can provide much information on the high- and (sometimes) low-temperature alloys; and (3) this approach has identified the origin for the novel special–point ASRO in AuFe. Displacement effects, i.e., non–rigid lattice effects, as well as the other contributions beyond band–energy, are being incorporated into the multicomponent alloy calculations. Such improvements will allow us to investigate other alloys, where charge effects may play a role, to "design", for example, higher temperature intermetallics through alloying.

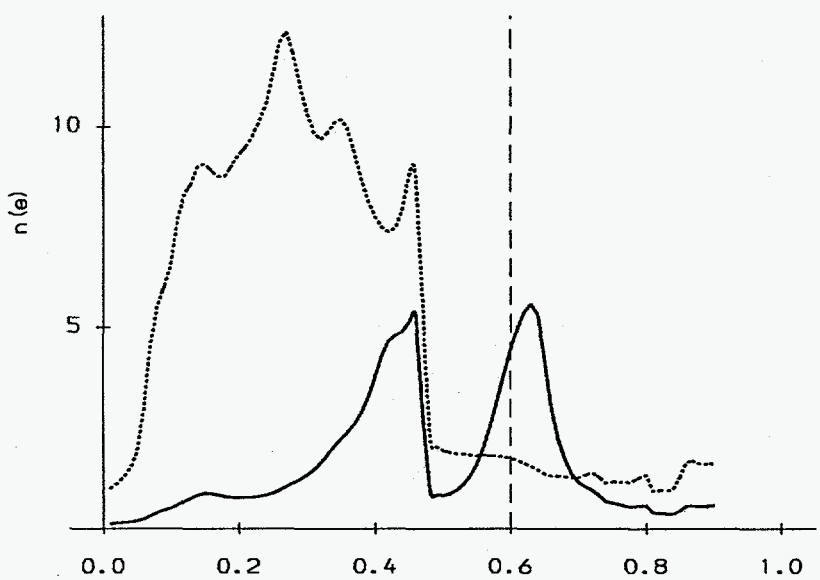


Figure 3. Compositionally– and orientationally–averaged DOS for DLM $Au_{75}Fe$ in states/Ryd-atom vs. Ryd. Contributions from Au (Fe) sites are given by dotted (full) curves.

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