Final Technical Report on "Intermetallic Alloys: Patterns and Complexity"

My research, funded by the DOE research award DE-FG02-93ER45495, has been geared towards the understanding of ordering in metallic alloys. My effort has been focused on analyzing the role of the coupling between structural and chemical degrees of freedom and its impact on the formation of ordered structures, and on the effects of geometrical frustration on ordering in simple spin models. Over the course of this project, I have had the support of three graduate students and two postdoctoral research associates who devoted half of their time to the project.

Significant Accomplishments

Interplay of chemical and structural correlations in alloys

Understanding the detailed structure of disordered metallic alloys is crucial to the study of phase stability in alloys. The coupling between atomic displacements and chemical short range order in disordered alloys is far from being well understood. Particularly interesting are alloys in which the constituent atoms have a large size mismatch. In an effort to elucidate the nature of correlations in such an alloy, a joint theoretical and experimental study of the 50-50 Cu-Au alloy was undertaken. Simulations based on an atomistic model derived from the effective medium theory (EMT) of bonding in metallic systems[1] were compared to experimental results[2]. An important advantage of real-space simulations is that they permit a direct examination of the relationship between local chemical environment and atomic displacements. The EMT based simulations showed a strong correlation between nearest-neighbor environment and interatomic distances. These correlations were more complex than that predicted from simple "size-effect" arguments. The simulations correctly reproduced the chemically specific nearest-neighbor distances in random alloys across the entire Cu_xAu_{1-x} concentration range. The nontrivial correlations between atomic displacements and chemical environment indicated that atomic displacements play a significant role in the ordering transition in these alloys. Specifically, any theory of ordering in these alloys have to take into account the coupling between the local chemical order and the local bond lengths.

Classical density-functional theory applied to ordering in alloys

A theory of ordering which takes into account the role of coupling to strain fields has been formulated by extending the ideas of classical density functional theory of liquids. Classical density functional theory (DFT) is an attractive approach to apply because of its success in describing the freezing transition in liquids and the application of a lattice gas version of DFT to order disorder transitions in alloys[3, 4]. One attraction of this theory is the possibility of using correlation functions obtained from first-principles calculations of disordered alloys. A lattice gas DFT has not been completely successful in predicting phase stability of alloys since elastic effects are expected to play a role, for example through overall density changes, even in transitions where the symmetry of the lattice does not change. An extension of the lattice gas formalism to include a global strain tensor along with the chemical occupation variables have been formulated[5] and applied to Cu_3Au and Ni_3V. This work has formed the basis of the PhD.D. thesis of my student David Olmsted.

The study of Cu_3Au was intended to be an internal self-consistency check of the extended lattice-gas DFT. Simulations of Cu_3Au, based on EMT were performed to provide correlation functions which were used as inputs to the DFT and the predicted phase

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diagram was compared to the one obtained from the EMT simulations[6]. The results showed that the coupling to the volume change had a significant effect on the two-phase regions, however, the DFT prediction for the discontinuity in the order parameter at the transition was significantly smaller than that observed in the simulations.

An advantage of EMT is that it can allow for arbitrary lattice distortions, and the DFT formalism in conjunction with correlation functions obtained from EMT has been applied to the ordering transition in CuAu which has a significant tetragonal distortion.

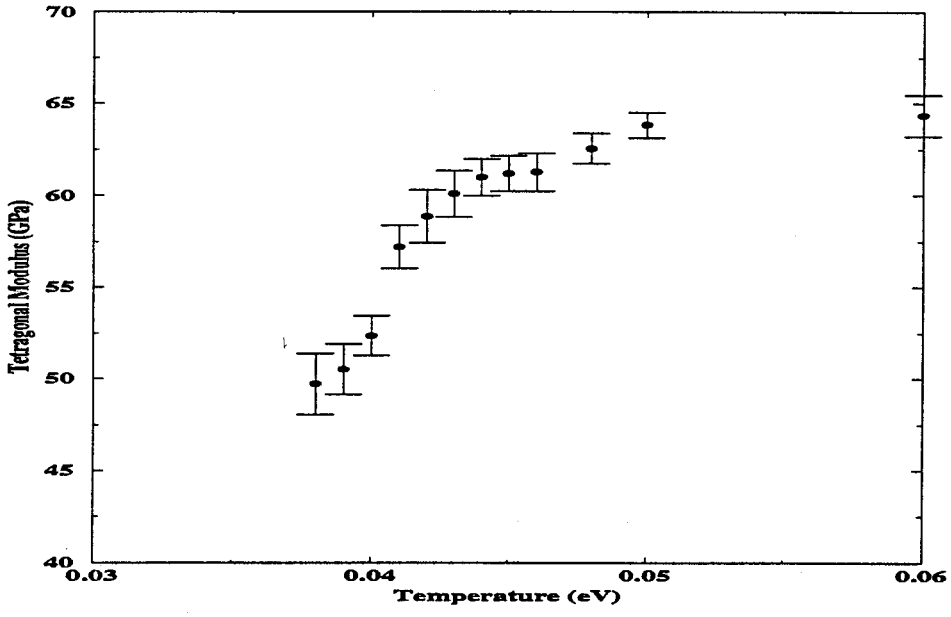

Figure 1: Plot of the elastic modulus which measures the strength of the lattice with respect to a volume conserving tetragonal distortion. The results show a remarkable softening as the first order transition temperature ($\approx 0.038eV$) is approached.

Elastic effects in CuAu

The 50-50 Cu-Au alloy has two first order phase transitions. Above 683K the stable phase is a face-centered-cubic (FCC) disordered phase. Below 658K the stable phase is CuAuI which is an ordered $L1_0$ phase with a 7% tetragonal distortion. Between these two temperatures, the stable phase is CuAuII which is a long-period superstructure with a modulation wave vector that is perpendicular to the ordering direction. We have used EMT extensively to study this alloy and these studies have shown that EMT provides a good description of the interactions in this alloy[2]. The work on short-range order[2] demonstrates that the EMT predictions of the pair-correlation functions are in good agreement with experiments. We have, therefore proceeded to use these correlation functions from the disordered alloy as inputs to the DFT formalism and analyze the effects of elastic distortions on the phase diagram around the stoichiometric composition. Our main interests are in the role played by the coupling of the chemical short-range order to the tetragonal distortion. We know that such a coupling exists from the Monte Carlo studies of the disordered state[2].

The inputs to the DFT formalism are the chemical pair-correlation function (or diffuse

scattering structure factor), $S^{(2)}(\mathbf{q})$, as a function of temperature and concentration and the elastic moduli corresponding to (i) volume changes (bulk modulus) and (ii) a volume-conserving tetragonal distortion[5]. All of these functions can be obtained from EMT simulations of the CuAu alloy. To predict ordering transitions as accurately as possible, these correlation functions should be measured in the disordered phase just above the ordering transition. These calculations were carried out by Sib K. Ghoshal, a postdoctoral research associate. Calculations of the elastic moduli show a remarkable softening of the lattice towards a volume-conserving tetragonal strain. We obtained this particular modulus by measuring the response of the alloy to a stress which couples to this type of tetragonal strain. The results are shown in Fig. 1. This type of softening is characteristic of a compressible, frustrated antiferromagnet[7] and these results provide further evidence of the relevance of these models to ordering of alloys on FCC lattices[8].

The softening of this tetragonal modulus is in contrast to the bulk modulus which remains essentially constant and is consistent with the correlation between short-range order and tetragonal fluctuations that was found in our earlier study[2]. The effects of elastic distortions on the phase diagram of CuAu is, therefore expected to be much more dramatic than that observed in Cu_3Au which has only a small volume distortion. We plan to map out the complete phase diagram (near 50-50 at. %) with special emphasis on two-phase regions and the degree of the ordering transitions. This work is being carried out in collaboration with David Olmsted who is now at Brown University and and we expect to complete this within the next few months.

Effective Theories

Construction of effective continuum theories from microscopic, atomistic models is an important ingredient in the multi-scale modeling that is essential for understanding pattern formation in alloys and their sensitivity to processing. A numerical scheme, based on Monte Carlo simulations has been applied to a frustrated spin model where the effective continuum model is known reasonably well. This application has shown that the method is remarkably successful in constructing continuum models starting from a microscopic Hamiltonian[9]. This scheme is now being applied to a spin model coupled to lattice distortions where the continuum theory is not well established.

Geometrical Frustration

The role played by geometrical frustration in ordering transitions was studied by analyzing a simple spin model which captures the essence of the EMT description of alloys such as CuAu. The study of both the statics and dynamics of the ordering transition in this model has been the topic of the PhD thesis of my student Lei Gu. An unusually interesting aspect of this study has been the observation of a dynamical transition which is reminiscent of the glass transition in supercooled liquids. Detailed analysis of the model has elucidated the role of defects in the glassy dynamics and the similarity between the transition observed in this model and the one observed in structural glasses[10].

The last graduate student to be supported by this grant, Hui Yin, continued the analysis of the model studied by Lei Gu and has obtained results that have had an impact on the area of structural glasses. His work has shown a connection between the presence of extended structures, an entropy vanishing transition and glassy dynamics[11, 12]. As a referee of one of these papers put it, the authors have "combined large scale simulations with exact results to paint a tangible picture exhibiting many features hypothesized in other papers about structural glasses". This has been the major success of Hui's work;

the identification and analysis of a tractable model of the glass transition. The analysis has, therefore, shed light on many of the mysteries of the glass transition in supercooled liquids.

Status of Students/Postdoctoral Associates

Hui Yin completed his PhD thesis in May, 2001 and is working in a company modeling Silicon device.

David Olmsted completed his PhD in 2000 and is a postdoctoral research associate at Brown University.

Lei Gu completed his PhD in 1999 and has been working in a software company.

Nicholas Gross was a part-time postdoctoral associate who is now a faculty member at Northeastern University.

Sib Ghoshal, another part-time postdoctoral associate has gone back to India and is a faculty member at Chandigarh University.

Publications resulting from this grant

"Slow dynamics and aging in a non-randomly frustrated spin system", Hui Yin and Bulbul Chakraborty, to appear in Phys. Rev. E

"Entropy-vanishing transition and glassy dynamics in frustrated spins", Hui Yin and Bulbul Chakraborty, *Phys. Rev. Lett.* **86**, 4058 (2001).

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