First-Principles Calculations of Cluster Densities of States and Short-Range Order in $Ag_c Pd_{1-c}$ Alloys

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Calculations of the densities of states associated with a particular local configuration of atoms in a substitutionally disordered alloy are reported. An application to Ag_cPd_{1-c} alloys yields detailed information about charge transfer and short-range order in these alloys.

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The primary theoretical tool for studying the electronic structure of substitutionally disordered alloys in recent years has been the coherent-potential approximation[1] (CPA). In the CPA, one calculates a translationally invariant effective medium by imposing the self-consistency condition that the scattering off of a real atom embedded in the medium vanishes on the average. The introduction of the translationally invariant CPA medium greatly simplifies the calculation of densities of states (DOS) in disordered alloys.

The earliest CPA calculations[2,3] were carried out within the framework of a tight-binding (TB) model. Since then the computational tools have been developed[4,5] for applying the CPA formalism to systems describable by nonoverlapping muffin-tin Hamiltonians. These calculational techniques are similar to those used in Korringa-Kohn-Rostoker[6,7] (KKR) calculations of DOS in pure metals. The TB CPA and the KKR CPA have been used successfully to calculate DOS and transport properties[8,9] of disordered substitutional alloys. It is now generally acknowledged that the KKR CPA provides a reliable, first-principles description of band structure and other properties of alloys and avoids the parametrizations used in the TB CPA.[10]

In spite of its many desirable properties, however, the CPA, as a single-site approximation, cannot be used to investigate local-environment effects which involve correlations among many sites. Such correlations play a crucial role in determining the structure of the DOS in disordered systems. Attempts to extend the CPA to a cluster, or multisite, approximation have proved to be either too difficult to implement computationally, such as the molecular CPA,[11] or lacking in analytical rigor.[12] Severe simplifications such as the substitution of a Cayley tree (or Bethe) lattice for the proper crystal structure of the material surrounding the cluster have been made in other work.[13] To this date, no *a priori* cluster DOS calculations based on the potential functions of an alloy and taking realistic account of local environment effects and of the proper crystal structure have been reported. It is the purpose of this Letter to report such calculations for the case of Ag_cPd_{1-c} substitutional alloys.

Our calculations are based on methods for treating a cluster of impurity atoms embedded in a translationally invariant medium. These methods have been completely developed[14] in connection with TB systems and extensive one-dimensional model calculations for such systems have been carried out.[15] We have generalized these methods to systems describable by muffin-tin Hamiltonians and have applied them to a cluster consisting of a central site and its shell of nearest neighbors embedded in a medium determined within the KKR CPA. The densities of states were obtained from the site-diagonal element of the Green's function associated with the center of the cluster, calculated by use of a generalization of the KKR CPA formulas given by Faulkner and Stocks.[5] An independent derivation of our formulas has recently appeared[16] in a treatment of a cluster of impurity atoms embedded in a pure host.

Figure 1(a) depicts the densities of states associated with a Pd atom surrounded by various configurations of Pd and Ag atoms in the first-neighbor shell. The DOS are plotted as a func-

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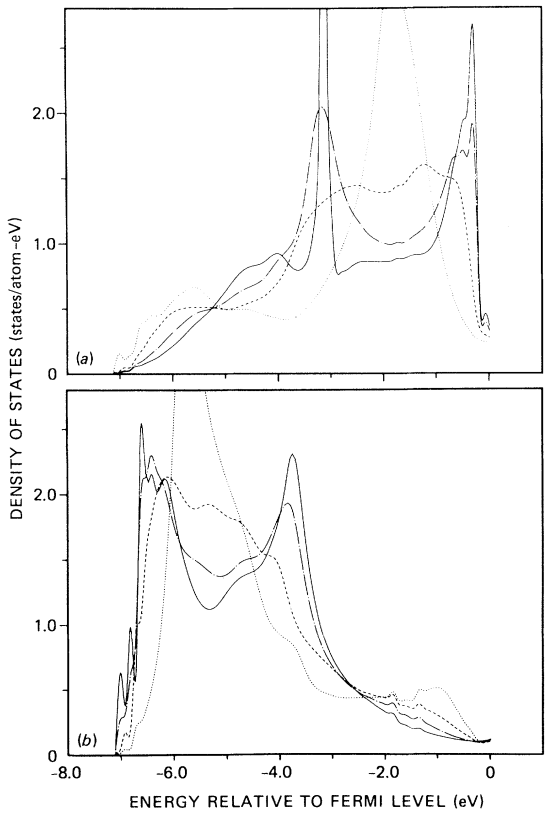

FIG. 1. (a) Density of states at the center of a Pd-centered near-neighbor (nn) cluster in a $Ag_{0.5}Pd_{0.5}$ alloy. Solid line, Pd surrounded by twelve Pd nn; dotted line, Pd surrounded by twelve Ag nn; dot-dashed line, Pd surrounded by ten Pd and two Ag nn with the Ag atoms second-nearest neighbors of each other; dashed line, Pd surrounded by six Pd and six Ag nn in an arbitrary configuration. These DOS are practically identical to those obtained in the CPA. (b) Results analogous to those of (a) but with the roles of Pd and Ag interchanged.

tion of energy with the Fermi level as determined in the KKR CPA taken as the zero of energy. It is seen immediately that cluster DOS can deviate substantially from those obtained in the single-site CPA. Note in particular that the DOS for the center of an all-Pd cluster (solid line) resembles that of pure Pd, while the DOS for a Pd atom surrounded by twelve Ag atoms displays the single peak (dotted line) characteristic of an impurity embedded in a pure medium. Clusters of composition between these two limits, for example the dash-dotted curve, yield DOS that move gradually from one to the other of the two curves corresponding to these extreme configurations. Figure 1(b) depicts results analogous to those of Fig. 1(a), but associated with an Ag atom at the

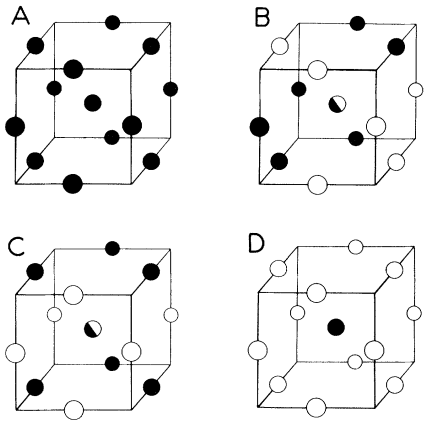

FIG. 2. Cluster configurations used in calculations of average central site energies. *A*, twelve like nn (clustering); all sites are either Ag or Pd. *B*, six like nn, six unlike nn (random): filled circles, Ag; open circles, Pd; half-filled circles, either Ag or Pd. *C*, six like nn, six unlike nn (some order); key same as *B*. *D*, twelve unlike nn (ordered): filled circles, Ag(Pd); open circles, Pd(Ag).

center of the cluster, rather than a Pd atom.

The potentials used in the calculation are those of Stocks and Winter[17,18] and are charge self-consistent within the CPA. Calculation of the total charges associated with the central sites of the various clusters reveals only a slight dependence on the occupancy of the near-neighbors shell. For the cluster labeled *B* (Fig. 2), which contains equal numbers of Ag and Pd sites distributed at random and as such is "most representative" of the random alloy, the charges obtained are almost identical with those obtained in the CPA.

Cluster densities of states lend themselves to an investigation of short-range order (SRO) and clustering in alloys. Experimental methods such as x-ray and neutron diffraction yield information about the tendency of atoms of a certain kind to surround themselves as much as possible by atoms of a different kind (SRO) or of the same kind (clustering). Calculations of total energies for different atomic arrangements can, in principle, distinguish between such tendencies. Although it should be possible in the foreseeable future to calculate the total energy for various configurations within local density theory, our present calculations include only the band energy and thus neglect certain "double-counting" terms of the Coulomb and exchange-correlation parts of the energy. Our belief (which appears to be supported by a growing amount of evidence[19-22])

is that the part of the energy which we include is by far the most important one for determining the structural properties of solids. Our neglect of these double-counting terms would likely be a poor approximation for a system with significant charge rearrangement. Fortunately (see Table I), the charge on an Ag or Pd atom is quite insensitive to the surrounding configurations. We have calculated, for various configurations, the average (band energy)/site $\langle E\rangle = C_A E_A{}^{\xi} + C_B E_B{}^{\xi}$, where $E_\alpha{}^{\xi}$ ($\alpha = A$ or B) is the band energy associated with the central atom of type α when surrounded by some particular configuration ξ of near neighbors. If $n_\alpha{}^{\xi}(\epsilon)$ is the corresponding central site density of states, the band energy is given by

$$E_\alpha{}^{\xi} = \int_{-\infty}^{\epsilon_F} \epsilon n_\alpha{}^{\xi}(\epsilon) d\epsilon, \quad (1)$$

where ϵ_F is the Fermi energy determined in the CPA.

In Table I, we show values of $\langle E\rangle$ for four near-neighbor shell configurations for the $Ag_{0.5}Pd_{0.5}$ alloy, shown explicitly in Fig. 2. For the configurations A, the central atom is surrounded by twelve like neighbors. These configurations are, therefore, representative of a clustering situation. In configurations B and C there are six like and six unlike neighbors, as in the random alloy. In configurations D the central site is surrounded by all unlike neighbors. These configurations are therefore representative of a SRO situation. The values of $\langle E\rangle$ shown in Table I indicate that unlike near neighbors are energetically favored over like near neighbors, i.e., we predict that $Ag_{0.5}Pd_{0.5}$ alloys would exhibit a tendency toward SRO rather than clustering. It is interesting that even for the isoatomic clusters B and C, the cluster which is most ordered lies lowest in energy. This tendency toward SRO is in accord with experiment. While x-ray data fail to indicate SRO in AgPd alloys because of the nearly equal scattering powers of Ag and Pd, the observed[23] negative heats of mixing of these alloys strongly indicate the presence of local order. This is in contrast to alloys with positive heats of mixing and exhibiting strong clustering tendencies, such as NiCu alloys. The difference in behavior may be due to the tendency toward the formation of magnetic moments in Ni-rich clusters while our calculations show that in AgPd even an all-Pd cluster would fail to form a moment. If we take the difference in energy between clusters B and D (2.6×10^{-2} eV ~ 300 K) to be indicative of the ordering temperature to be expected, this would be consistent with the fact that while resistivity measurements fail to indicate the presence of an ordered phase they are suggestive of either SRO or cluster formation for long anneals at temperatures around 550 K.[24] At temperatures below this where an ordered phase may be expected, its formation is presumably prevented by slow diffusion rates.

The primary approximation in our calculations is the use of Eq. (1) to determine the energy differences between configurations. In addition, we have not made the potential functions self-consistent for each cluster configuration. Both of these approximations are readily removed at the expense of heavier computational effort. However, until such calculations are completed, our results for the magnitude of the small energy differences between configurations in AgPd al-

TABLE I. Central site charges Q and average site energies $\langle E\rangle$ for various near-neighbor (nn) shell configurations in a $Ag_{0.5}Pd_{0.5}$ alloy. Cluster C is more ordered than cluster B in the sense that its symmetry is higher and there are more AgPd nn bonds. The last row gives the charges calculated with the CPA.

Cluster type; configuration	Q (electrons/atom) Ag	Pd	Ave.	$\langle E\rangle$ relative to type A (10^{-2} eV)
A; twelve nn	10.828	10.093	10.461	0.0
B; six like nn, "random"	10.938	10.068	10.503	−6.5
C; six like nn, "some ordering"	10.952	10.088	10.520	−8.0
D; no like nn	11.010	10.042	10.526	−9.1
CPA	10.943	10.057	10.500	

loys should be viewed as indicative rather than definitive.

Clearly the methods we have outlined in this Letter not only offer a way of going beyond the CPA by allowing the incorporation of the effects of SRO and clustering on the electronic structure, but also provide an *ab initio* framework within which to explore problems of current interest such as the construction of metallurgical phase diagrams and transport properties.

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