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Order-disorder transformations in noble-metal binary alloys

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A band theory for order-disorder phase transformations introduced previously by the authors is applied to CuAg and AgAu, neither of which is observed to order experimentally. Our results place limits on the validity of a simple *s*-band model for the Fermi-level-derived ordering energies in the noble-metal binary alloys.

In this Comment we would like to present results of further applications of the band theory for order-disorder transitions introduced by us in a previous article.[1] The new results illustrate the limits of a simple *s*-band electronic theory for the ordering energy of the noble-metal binary alloys.

The first application of our theory[1] was to the order-disorder transition of CuAu. We believed the ordering energy to be primarily a Fermi-level effect. For the noble metals, the simplest electronic theory giving sensible densities of states at the Fermi level is one with a single *s* band. This model neglects the effects of the *d* bands which contribute to Fermi-level properties through hybridization. Nonetheless, the use of the single-*s*-band model allowed us to predict a transition temperature of 555 K for CuAu compared with the experimental value of 683 K. The theory also predicted temperature-dependent long- and short-range order and internal energy in better agreement with experiment than a comparable Ising theory.

In a later work[2] we tested the limits of this *s*-band theory by performing analogous calculations for Cu_3Au and $CuAu_3$, both of which also exhibit order-disorder transformations. In that case the theory predicted that both alloys should have a transition temperature of $\sim$ 467 K. The Ising model with concentration-independent nearest-neighbor pair interactions also predicts an equality of the transition temperatures. The value of 467 K is in excellent agreement with the experimental value of 473 K for $T_c(CuAu_3)$ but is quite low compared with the value of 663 K for $T_c(Cu_3Au)$. It was concluded that the observed asymmetry between the order-disorder phenomena of these two alloys is primarily related to different atomic volumes. Since the volume dependent properties of the transition and noble metals are determined mainly by the *d* bands, it was suggested that a more elaborate calculation taking both *s* and *d* bands into account would be necessary to improve agreement between theory and experiment.

In this Comment we report results of applications of the *s*-band model to AgAu and CuAg which further test its validity for the noble-metal binary alloys. Both applications are null tests in the sense that neither AgAu nor CuAg order.[3] The phase diagrams show that Cu and Ag are almost immiscible below the eutectic at 1052 K while the Ag-Au alloys are completely miscible. The AgAu alloy does not exhibit long-range order at low temperatures, although considerable short-range order correlations have been observed. This experimental result places an upper limit of a few hundred kelvin on the ordering temperature. Such a low transition temperature would require extremely long annealing times in order to achieve an ordered state.

The same electronic theory was used for the ordering energies of CuAg and AgAu as was used for the CuAu application.[1] The input parameters to the calculation were chosen as follows. The differences δ between the centers of gravity of the *s* bands in the pure metals was taken as the difference between ionization energies of the atoms.[4] The bandwidths in pure Cu, Ag, and Au were taken from band-structure calculations[5] as the $\Gamma \rightarrow W_3$ energy. All other aspects of the calculations were identical to the CuAu application, including the assumption of an ordered state of $L1_0$ symmetry. This symmetry and our method of calculation guarantee that a first-order transition must take place.

The transition temperature of CuAg was calculated to be less than 10 K, the limit of numerical accuracy in the calculations. This negligible value of T_c is consistent with the immiscibility of Cu in Ag for all but very small solute concentrations. The theoretical result is a consequence of the small values of δ (0.15 eV) and its ratio to the typical bandwidth of $\sim$14 eV. The transition temperature scales as the bandwidth (W) and is a maximum with respect to δ when $\delta/W \sim 1$.

The transition temperature of AgAu was calculated as 765 K. This value is greater than the value of 555 K calculated for CuAu. Relative to CuAu, the input value of δ in AgAu is larger and the average bandwidth is smaller.

Our model predicts the self-consistent *s*-electron charge transfer to the Au site in random AgAu to be 0.14 *e*/at. This value is comparable to the value of ~0.12 *e*/at. obtained by Gelatt and Ehrenreich[6] in a two-band (*s* and "*d*") coherent-potential-approximation calculation for this alloy. In their calculation it was found, however, that the *d*-electron charge transfer was of the opposite sign to the *s*-electron transfer. This reduced the total charge transfer to 0.069 *e*/at. They argued that this value was sufficiently small to give an ordering temperature less than 200 °C. based on Mott's Madelung energy arguments,[7] i.e., sufficiently small that the ordering could not be observed experimentally. This assumes of course that the charge transfer does not vary with the order in the alloy—a conclusion we do not find to be the case in our calculations.

The results of the AgAu calculation point out the limits of the simple *s*-band model. Though nearly full, the *d* bands do seem to play an important role in determining the ordering energy of the noble-metal binary alloys. There seems to be no simple model of how the *d* bands could act to "quench" the ordering energy in AgAu but not in CuAu. The energy gap between the "top" of the *d* band and the Fermi level is the optical gap of the noble metals and ranges[8] from 2.1 eV in Cu and 2.5 eV in Au to 3.9 eV in Ag. A linear interpolation with concentration predicts a gap ~0.8 eV larger in AgAu and CuAg than in CuAu. This suggests that the *d* bands should play less of a role in affecting the ordering energy of the Ag-based alloys than in CuAu. It is worth noting however that the Ag *d* bands are considerably different from the other two metals, and that the Ag-based alloys are the ones which do not order.

The *d* electrons are highly correlated and the atomic-volume difference between AgAu and CuAu is most likely a factor crucial to understanding why AgAu does not order. Our calculation did not explicitly include any volume dependence to the matrix elements determined from the pure materials. The fractional volume difference between AgAu and CuAu is about the same as that between Cu_3Au ($T_c = 663$ K) and $CuAu_3$ ($T_c = 473$ K). We have argued previously[2] that semiclassical volume-dependent nearest-neighbor effective ion-ion interactions and the Ising model do predict approximately the correct transition-temperature ratio between these latter two alloys. The same arguments predict a similar ratio of ~0.7 for $T_c(\text{AgAu})/T_c(\text{CuAu})$ due to the smaller atomic volume of CuAu. Though the first-nearest-neighbor interaction should drop off rapidly with distance, more complete theories of the interactions suggest that they are of longer range due to Friedel-like oscillations.[2,9]

Clearly a more complete understanding of the interplay between these different effects in determining the order-disorder phenomena of the noble-metal binary alloys will require an electronic theory which takes full account of the *s* and *d* bands, as well as volume changes.

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[1] R. C. Kittler and L. M. Falicov, Phys. Rev. B 18, 2506 (1978).

[2] R. C. Kittler and L. M. Falicov, Phys. Rev. B 19, 291 (1979).

[3] M. Hansen, *Constitution of Binary Alloys*, (McGraw-Hill, New York, 1958).

[4] C. E. Moore, *Atomic Energy Levels* (U.S. GPO, Washington, D.C., 1958).

[5] G. A. Burdick, Phys. Rev. 129, 138 (1963); N. E. Christensen, Phys. Status Solidi B 31, 635 (1969); N. E. Christensen and B. O. Seraphin, Phys. Rev. B 4, 3321 (1974).

[6] C. D. Gelatt and H. Ehrenreich, Phys. Rev. B 10, 398 (1974).

[7] N. F. Mott, Proc. Phys. Soc. Lond. 49, 258 (1937).

[8] D. Beaglehole and E. Erlbach, Phys. Rev. B 6, 1209 (1972).

[9] R. J. Harrison and A. Paskin, in *Metallic Solid Solutions* edited by J. Friedel and A. Guiner (Benjamin, New York, 1963).