Pinski et al. reply

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Pinski et al. Reply: With our calculations [1], we uncovered the electronic mechanism responsible for inducing atomic short-range order (SRO) in the disordered solid solution of NiPt as it is cooled. Usually, but not always, SRO, whether derived theoretically or measured experimentally, indicates the nature of the long-range-ordered (LRO) state that will stabilize at low temperature. Our calculation of the atomic SRO, while agreeing with experiments [2], neglected the relativistic effects in the electronic structure. Lu, Wei, and Zunger (LWZ) [3,4], on the other hand, have calculated the L1_0-ordered alloy formation energy and find that only when relativistic effects are included is the L1_0-ordered phase lower in energy than the phase-separated state.

Before we continue, we define three energy differences. The first is the ordered-alloy formation energy $E_o$, which is defined as

$$E_o = E(L1_0) - (E_A + E_B)/2,$$

where $E(L1_0)$ is the energy of the ordered $L1_0$ state and $E_A$ and $E_B$ are the energies of the pure elements A and B (in this case Ni and Pt). The second is the disordered-alloy formation energy $E_d$, given by

$$E_d = E(\text{disordered}) - (E_A + E_B)/2,$$

where $E(\text{disordered})$ is the energy of the disordered state. Finally, the third energy, the ordering energy $\Delta E$, is simply the difference of these two energies:

$$\Delta E = E_o - E_d.$$

Both $E_o$ and $\Delta E$ are sometimes called ordering energies. The first, $E_o$, considers the difference in energy between the ordered $L1_0$ phase and the phase-separated elements. The other, $\Delta E$, is the energy difference between the ordered and disordered phases. In our paper [1], we did not calculate $E_o$ nor $E_d$. We looked at the electronic origins of the SRO that can be related to the finite temperature generalization of $\Delta E$. LWZ [3,4] only considered $E_o$, albeit for a different set of volumes. We have since calculated $E_d$ and found that it has the same behavior as LWZ [4] found for $E_o$: negative when relativistic effects are included and positive without them.

LWZ [3,4] indicated that relativistic effects are important in the calculation of the ordered-alloy formation energy. We agree, but point out that the same features responsible for lowering the ordered ($L1_0$) energy will also lower the energy of the disordered state. The shift to lower energies of the s bands, when relativity is included, is common in both phases. They have determined the origin of the ordered-alloy formation energy but they cannot address questions that differentiate between the ordered and disordered states. We found [1] that the bonding differences between ordered and disordered states come from d-hybridization effects in the valence bands and are virtually unaffected by relativity.

Questions regarding the role of size mismatch can now be addressed. Size mismatch can influence $E_o$ and $\Delta E$ in different ways. In our view, there are two effects in operation here. The first is given by the Hume-Rothery 15% rule, which permits mixing if the size difference is not too large [5]. This is what LWZ [3,4] uncovered in their calculations. However, in discussing ordering, we are addressing a second effect: If the two species mix, the tendency to form superlattices increases with increasing differences in atomic diameters [5]. As discussed in [1], this second type does not require a relativistic treatment of the underlying quantum mechanics.

To summarize, our calculations, based on a first-principles Landau theory, probe the local stability of the disordered state and may miss some of the features dealing with the global stability of all phases since terms beyond second order have been omitted. In most metallic alloys, the short-range order at elevated temperatures is usually a precursor of the state that develops as the temperature is lowered. In the case of NiPt, since ordering is a second-order transition, the fluctuations above the transition temperature must reflect the nature of the low-temperature ordered state. Thus, the calculations presented in the two papers ([1] and [3]) give complementary information and are not incompatible despite the claims of Lu, Wei, and Zunger.

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