Comment on "Origins of Compositional Order in NiPt Alloys"

d-band filling arguments suggest that all alloys of late transition metals will phase separate (rather than order) at low temperature since the antibonding part of the d band is nearly filled. Understanding the physical origins of the *exceptions* to this rule—most notably the observed $L1_0$ long-range ordering of NiPt—has been the focus of a number of recent investigations [1,2].

A necessary condition for long-range order (LRO) is that the formation enthalpy of the ordered phase o,

$$\Delta E_o(V_\sigma, V_A, V_B) = E_o(V_\sigma) - \tfrac{1}{2}[E_A(V_A) + E_B(V_B)],$$

be negative. Here, E_a is the total energy of a and V_σ, V_A, and V_B denote the equilibrium volumes of the 50%-50% phase and of its pure constituents (here, A is Ni and B is Pt). This equation can also be written as

$$\Delta E_o(V_\sigma, V_A, V_B) = \Delta E_o(V_\sigma, V_\sigma, V_\sigma) + \Delta E_{VD},$$

where the first term denotes the energy difference in the hypothetical situation where the ordered phase and its constituents all adopt the 50%-50% volume V_σ, while the second term is the "volume deformation" (VD) energy [3] associated with deforming $E_A(V_A)$ to $E_A(V_\sigma)$ and similarly for B. The mixing enthalpy of the disordered (d) phase ΔE_d can be written analogously.

Using the concentration wave (CW) method, Pinski *et al.* [1] calculated the short-range-order (SRO) parameter of $Ni_{0.5}Pt_{0.5}$, which is related to the finite-temperature "ordering energy" $\delta E = \Delta E_o - \Delta E_d$ at constant volume V_σ. They found that the high-temperature *disordered* alloy shows a (100)-ordering wave. They proceeded to conclude that this SRO also explains the observed (low-temperature) $L1_0$-type (100) LRO, giving also their calculated order-disorder transition temperature. They concluded that (i) the effects of relativity can be neglected for the purpose of understanding the origins of the $L1_0$ LRO in this system and that (ii) the large size mismatch between Ni and Pt is the dominant effect leading to $L1_0$ ordering. While we have also calculated δE for many systems [3] and have no argument with their discussion of SRO effects underlying δE, we show here that δE has no bearing on the LRO when ΔE_{VD} is large. We find that both of their conclusions on LRO based on δE are incorrect: (i) Relativity is the sole reason for LRO in NiPt and (ii) size mismatch, although favoring SRO [3], *discourages* LRO.

In the currently practiced CW approach [1] one assumes that concentration fluctuations *do not alter the volume* V; hence the relaxation energy ΔE_{VD} (and its response functions) is neglected. The SRO can be a valid predictor of LRO only when the constituents have nearly equal atomic sizes; only then can the energy response towards positional relaxations be neglected. This condition is not met for $Ni_{0.5}Pt_{0.5}$ whose constituents have a very

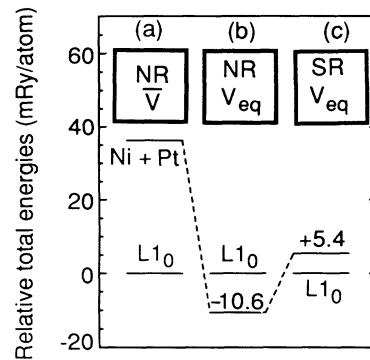FIG. 1. Nonrelativistic (NR) and scalar-relativistic (SR) LAPW-calculated total energies at the equilibrium (eq) volumes and at the $Ni_{0.5}Pt_{0.5}$ volume $\bar{V} = V_\sigma$.

large size mismatch (11%). Figure 1(a) shows our linearized-augmented-plane-wave- (LAPW-) calculated *nonrelativistic* (NR) total energy of the ordered $L1_0$ phase of NiPt and that of an equivalent amount of the constituents, all kept at $V_\sigma = V_{expt}(Ni_{0.5}Pt_{0.5})$. It shows that when ΔE_{VD} is neglected, $\Delta E_o^{NR}(V_\sigma, V_\sigma, V_\sigma) < 0$. Hence, the nonrelativistic ordered $L1_0$ phase is more stable than phase separation into *strained*, nonequilibrium constituents. However, Fig. 1(b) shows that relaxation lowers enormously the energy of Ni and Pt (i.e., $\Delta E_{VD} \gg 0$) so that $\Delta E_o^{NR}(V_\sigma, V_A, V_B) > 0$. Hence, in contrast to Pinski *et al.* [1], phase separation, not ordering, is the true *nonrelativistic* LRO ground state of NiPt [2] even though the high-temperature disordered phase can exhibit SRO [1]. Figure 1(c) further shows that only relativistic effects stabilize the globally ordered phase over phase separation, i.e., $\Delta E_o^R(V_\sigma, V_A, V_B) < 0$. This sign reversal of the formation enthalpy is caused by a relativistic reduction in ΔE_{VD} [Fig. 1(c)] through a contraction of the Pt atom [2].

We conclude that in the presence of a significant size mismatch ($\Delta E_{VD} \gg 0$), the physics of the constant-volume "ordering energy" δE is irrelevant to LRO; the small-amplitude limit of the SRO as calculated by Pinski *et al.*'s CW method neglecting relaxational fluctuations is not predictive of LRO.

Z. W. Lu, S.-H. Wei, and Alex Zunger
National Renewable Energy Laboratory
Golden, Colorado 80401

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