Spin-polarization-induced structural selectivity in Pd$_3$X and Pt$_3$X (X = 3d) compounds

Z. W. Lu,a Barry M. Klein,a and Alex Zungerb

aDepartment of Physics, University of California, Davis, California 95616
bNational Renewable Energy Laboratory, Golden, Colorado 80401
(Submitted to Physical Review Letters on 20 December 1994)

Spin-polarization is known to lead to important magnetic and optical effects in open-shell atoms and elemental solids, but has rarely been implicated in controlling structural selectivity in compounds and alloys. Here we show that spin-polarized electronic structure calculations are crucial for predicting the correct $T = 0$ crystal structures for Pd$_3$X and Pt$_3$X compounds. Spin-polarization leads to (i) stabilization of the $L1_2$ structure over the $DO_{22}$ structure in Pt$_3$Cr, Pd$_3$Cr, and Pd$_3$Mn, (ii) to the stabilization of the $DO_{22}$ structure over the $L1_2$ structure in Pd$_3$Co and to (iii) ordering (rather than phase-separation) in Pt$_3$Co and Pd$_3$Cr. The results are analyzed in terms of first-principles local spin density calculations.

PACS numbers: 61.66.Dk, 71.20Cf, and 75.50.Cc

Crystal structure compilations reveal that the most commonly occurring structures among intermetallic binary compounds with a 3:1 stoichiometry ($A_3B$) are the cubic $L1_2$ and the tetragonal $DO_{22}$ (Fig. 1). The crystallographic difference between the $L1_2$ and $DO_{22}$ structures is rather subtle: the two structures have identical first neighbor coordination (each $A$ has 8A + 4B neighbors and each $B$ has 12A neighbors) while a difference exists in the second shell (see Fig. 1). The manner in which particular $A_3B$ compounds select the $L1_2$ or the $DO_{22}$ configuration appears to be rather interesting. For example, the 4d trialuminides $A_3M$ show the sequence $L1_2 \rightarrow L1_2 \rightarrow DO_{22}$ as $M$ varies across the 4d row $Y \rightarrow Zr \rightarrow Nb$, while the 3d palladium alloys Pd$_3$X show $L1_2 \rightarrow L1_2 \rightarrow DO_{22} \rightarrow L1_2 \rightarrow L1_2$ as one proceeds in the 3d row $X = Sc \rightarrow Ti \rightarrow V \rightarrow Cr \rightarrow Mn \rightarrow Fe$ (for $X = Co$ and Ni, the systems phase-separate). The origin of such regularities was the subject of numerous investigations including the d-electron “generalized perturbation method” (GPM), and first-principles calculations. However, these calculations failed to reproduce the observed structural trends. These calculations were non-magnetic (NM, i.e., without spin-polarization). This appeared to be a reasonable assumption, since one expects that an alloy rich in a non-magnetic component (e.g., Pd$_3$Cr) or one without any magnetic components (e.g., Pd$_3$V) will not have any significant magnetic effects. We demonstrate here that spin-polarization have a crucial influence on the structural stability of Pd$_3$X and Pt$_3$X compounds: it stabilizes the observed $L1_2$ structure over the $DO_{22}$ structure in Pt$_3$Cr, Pd$_3$Cr, and Pd$_3$Mn, the $DO_{22}$ structure over the $L1_2$ structure in Pd$_3$Co, and is responsible for compound formation (rather than phase-separation) in Pt$_3$Co and Pd$_3$Cr.

The key insight to stability in compounds and alloys has traditionally been the association of stability with low density of states (DOS) at Fermi energy $E_F$. Nicholson et al. noted that for transition metal aluminides the more stable of the two structures ($L1_2$ or $DO_{22}$) corresponds to the one with smaller DOS at the Fermi-level, $N(E_F)$. Local density approximation (LDA) band structure and total energy calculations have later substantiated this relation. To examine such a relation for inter-transition metal $A_3B$ compounds rather than aluminides we have calculated $N(E)$ (Fig. 2) and total energy difference $\delta E = E(L1_2) - E(DO_{22})$ (Fig. 3(a) and Table 1) for Pd$_3$X with 3d atom $X = Sc$ through Cu using the NM linearized augmented plane wave (LAPW) method. We see that the structure with the lower calculated NM total energy (Table 1) indeed has a lower calculated NM $N(E_F)$ (Fig. 2), thus substantiating the underlying trends for aluminides. For example, for Pd$_3$X with $X = V$, Cr, and Mn, the Fermi energy, $E_F$, falls near a DOS maximum for $L1_2$ but near a DOS mini-
mum for \( DO_{22} \); correspondingly \( E(DO_{22}) \) is lower than \( E(L1_2) \). Unfortunately, while the magnitude of \( N(E_F) \) is indicative of the stability of the calculated structure, these non-magnetic calculations incorrectly predict the observed stable crystal structure in several cases: while \( Pd_3V \) is correctly predicted to be more stable in the \( DO_{22} \) structure, the observed \( L1_2 \) stable structure for \( Pd_3Cr \), \( Pd_3Mn \), \( Pd_3Fe \) and \( Pd_3Fe \) is the \( L1_2 \) structure, not the non-magnetically predicted \( DO_{22} \) structure. Thus, while the correlation between the calculated quantities \( N(E_F) \) versus \( E(L1_2) - E(\text{DO}_{22}) \) holds, it leads to incorrect predictions for the stability of \( Pd_3Cr \), \( Pd_3Mn \), and \( Pd_3Fe \). The generalized perturbation method calculations, \( \delta E \) based on similar DOS arguments (diamond symbols in Fig. 3(a)) likewise predicts \( Pd_3Cr \), \( Pd_3Mn \), and \( Pd_3Fe \) (and even \( Pd_3Sc \) and \( Pd_3Ti \)) to be stable in the \( DO_{22} \) structures, in conflict with experiment. \( \delta E \) In this paper we explain this puzzle by noting that while a large \( N(E_F) \) indeed implies a destabilizing factor for the one-electron ("band") energy, it also leads (in open-shell systems) to spin-polarization and magnetic moment formation which, in turn, is a stabilizing factor. Thus, despite their large \( N(E_F) \) in the \( L1_2 \) structure (suggesting one-electron instability), \( Pt_3Cr \), \( Pd_3Cr \) and \( Pd_3Mn \) (nearly so for \( Pd_3Fe \)) are correctly predicted to be more stable in this structure once spin-polarized total energy calculations are done. Thus, magnetic ordering changes the predictions of NM total energy calculations and restores agreement with experiment.

We have calculated the total energies of \( Pd_3X \), for \( X = \text{Sc through Cu} \) as well as \( Pt_3Cr \) and \( Pt_3Co \) in the \( L1_2 \) and \( DO_{22} \) structures using the LDA in both the spin-polarized and spin-unpolarized versions of the full-potential LAPW method. \( \delta E \) In order to accurately obtain the small energy difference between two fairly similar crystal structures, the calculations were carried out consistently using the same muffin-tin radii, \( R_{MT} \), and basis set energy cutoffs, \( K_{\text{max}} \). The Brillouin Zone summations were done using the geometrically equivalent k-point sampling scheme \( \{3\}^4 \) in which 20 (40) k-points in the irreducible zone for the \( L1_2 \) \( (DO_{22}) \) structure is mapped into the same 60 special k-points \( \{3\}^4 \) in the fcc structure. We optimized the total energy as a function of volume, as well as the \( c/a \) ratio in the \( DO_{22} \) structure. The estimated LAPW error for the \( E(L1_2) - E(\text{DO}_{22}) \) energy difference is \( \sim 5 \text{ meV/atom} \), and the neglected zero-point energy difference between the two similar structures should be even smaller. At zero temperature, the absolute stability of a compound in a structure \( \sigma \) with respect to phase separation is given by its formation enthalpy \( \Delta H(\sigma) \).

TABLE I. LDA calculated total energy difference (in meV/atom) \( \delta E = E(L1_2) - E(\text{DO}_{22}) \) and the ferromagnetic (FM) DOS at Fermi energy \( N(E_F) \) (in states/eV spin) for the \( L1_2 \) and \( DO_{22} \) structures. Note that the spin-polarization (included in the FM state) reverses the relative stability of non-magnetic (NM) \( L1_2 \) and \( DO_{22} \) structures for those compounds marked by an asterisk, thus restoring agreement with experiment. \( \delta E \). PS denote phase-separation.

| Structure | \( \delta E_{\text{NM}} \) | \( \delta E_{\text{FM}} \) | \( N_{\text{FM}}(E_F) \) | \( N_{\text{FM}}(E_F) \) |
|-----------|----------------|----------------|----------------|----------------|
| Pd3Sc     | \( L1_2 \) -102 | -102           | 0.34           | 0.65           |
| Pd3Ti     | \( L1_2 \) -48  | -48            | 0.14           | 0.28           |
| Pd3V      | \( DO_{22} \) 74 | 40             | 0.64           | 0.38           |
| Pd3Cr*    | \( L1_2 \) 74   | 20             | 0.57           | 0.60           |
| Pd3Mn*    | \( L1_2 \) 48   | 48             | 0.59           | 0.80           |
| Pd3Fe*    | \( L1_2 \) 14   | 1              | 0.42           | 0.34           |
| Pd3Co*    | PS              | -5             | 0.79           | 0.46           |
| Pd3Ni     | PS              | -2             | 0.95           | 0.93           |
| Pd3Cu*    | \( L1_2 \) -8   | -8             | 0.52           | 0.92           |
| Pt3Cr*    | \( L1_2 \) 71   | -23            | 0.56           | 0.54           |
| Pt3Co     | \( L1_2 \) -11  | -16            | 0.66           | 0.65           |

FIG. 2. LDA calculated NM total DOS for \( Pd_3X \) in the \( L1_2 \) and \( DO_{22} \) structures. The inserts denote \( N(E_F) \). An asterisk denotes the more stable structure predicted by total energy calculations in the absence of magnetic ordering. Note that the more stable structure has a lower \( N(E_F) \).
\( \Delta H_\alpha (\sigma) = E_\alpha (\sigma) - x_A E_A (V_A) - x_B E_B (V_B) \)  

where \( E_A (V_A) \) and \( E_B (V_B) \) are the energies of the constituents A and B in their respective ground states (e.g., for Pd_{3}Ni, it is non-magnetic fcc for Pd and ferromagnetic fcc for Ni). \( E_\alpha (\sigma) \) is the energy of structure \( \sigma \), \( \alpha = \text{NM or FM} \) denotes whether structure \( \sigma \) is in the non-magnetic or ferromagnetic states. The relative stability of two different ordered structures is,

\[
\delta E_\alpha = E_\alpha (L1_2) - E_\alpha (DO_{22}) \tag{2}
\]

while the magnetic stabilization energy of a given structure \( \sigma \) (\( L1_2 \) or \( DO_{22} \)) is

\[
\delta M(\sigma) = E_{FM}(\sigma) - E_{NM}(\sigma) \tag{3}
\]

Table I and Fig. 3(a) give \( \delta E_{NM} \) and \( \delta E_{FM} \), while Fig. 3(b) shows the magnetic stabilization energies \( \delta M(L1_2) \) and \( \delta M(DO_{22}) \), and the local magnetic moment \( \mu_X \) on the X atom calculated numerically within the muffin-tin sphere (the value of \( \mu_X \) is rather insensitive to the small change in muffin-tin radius).

![Figure 3](image)

**FIG. 3.** (a) LDA (present) and GPM (Ref. 1) calculated energy difference \( \delta E = E(L1_2) - E(DO_{22}) \) [Eq. (3)] for Pd_{3}X compounds. Note the reversal of sign for \( \delta E \) due to spin-polarization for Pd_{3}Cr, Pd_{3}Mn, and Pd_{3}Co (nearly so for Pd_{3}Fe). Part (b) gives the magnetization energies \( \delta M(\sigma) = E_{FM}(\sigma) - E_{FM}(\sigma) \) [Eq. (3)] for \( \sigma = L1_2 \) (empty circles) and \( \sigma = DO_{22} \) (solid squares) structures and shows the local magnetic moment for the X atom (numbers above or below the symbols).

Table II gives the formation enthalpies \( \Delta H_\alpha (L1_2) \) and \( \Delta H_\alpha (DO_{22}) \) for several systems. Figure 2 depicts the NM total DOS for Pd_{3}X, where \( X = \text{Sc} \rightarrow \text{Cu} \), in the \( L1_2 \) (left panel) and \( DO_{22} \) structures (right panel). One notices the following:

(i) In contrast to the very similar DOS for the \( L1_2 \) and \( DO_{22} \) structures and the small energy difference \( E(L1_2) - E(DO_{22}) \sim 20 \text{ meV/atom} \) predicted by the GPM, one sees from Fig. 2a a marked difference of the DOS in the \( L1_2 \) and \( DO_{22} \) structures. (a) While the DOS of the cubic \( L1_2 \) structure resemble that of fcc Pd, having three major peaks, the DOS of the \( DO_{22} \) structure are more smeared, reflecting a loss of cubic symmetry in the \( DO_{22} \) structure. (b) The DOS of the more stable \( L1_2 \) structure for Pd_{3}Sc and Pd_{3}Ti shows a “pseudo-gap” near the Fermi level absent in the \( DO_{22} \) structure. (c) In the \( L1_2 \) structure, the Fermi level of Pd_{3}V, Pd_{3}Cr, and Pd_{3}Mn falls on a DOS peak (made mostly of \( d \) orbitals of the X atom), while in the \( DO_{22} \) structure the Fermi level falls on a relatively flat portion of the DOS. Indeed, these materials are more stable in the \( DO_{22} \) structure in a NM LDA description. As a result of these differences, the values of the \( N(E_F) \) (given in the inserts of Fig. 2) and its shape near the Fermi level are strikingly different for the \( L1_2 \) and \( DO_{22} \) structures.

(ii) The above noted trends in the NM \( N(E_F) \) induce a concomitant magnetic stabilization energy \( \delta M \) [Fig. 2(b)] : A larger energy stabilization \( \delta M \) due to spin-polarization relates with a larger \( N(E_F) \) and with a larger localized magnetic moment \( \mu_X \) on the X atom [Fig. 2(b)]. For example, while the Pd_{3}X compounds with \( X = \text{Sc}, \text{Ti}, \text{Cu} \) are non-magnetic (so \( \mu = 0 \)), when \( X = \text{Mn} \) and \( \text{Fe} \), one sees in Fig. 2(b) large energy lowering due to spin-polarization (\( \delta M \sim -200 \text{ meV/atom} \)), and concomitantly large magnetic moments of 3.5 \( \mu_B \) (\( X = \text{Mn} \)) and 3.1 \( \mu_B \) (\( X = \text{Fe} \)) in both the \( L1_2 \) and \( DO_{22} \) structures (as a comparison, bcc Fe has a magnetic moment value of only 2.2 \( \mu_B \)). Thus, spin-polarization induces a local magnetic moment on the “magnetic” 3d-atoms with large NM \( N(E_F) \) while lowering the total energy of the compound. In the case of Pt_{3}Cr in the \( L1_2 \) structure for which previous calculation exists, our calculated total magnetic moment in the unit cell (2.6 \( \mu_B \)) agrees with a

**TABLE II.** Non-magnetic (NM) and Ferromagnetic (FM) formation enthalpies \( \Delta H \) [in meV/atom, Eq. (1)], of some compounds. \( \Delta H \)'s are taken with respect to the NM fcc Pd, Pt, FM fcc Ni, FM fcc Co, and anti-FM bcc Cr, respectively.

|          | \( \Delta H(L1_2) \) | \( \Delta H(DO_{22}) \) |
|----------|------------------------|------------------------|
| Pd_{3}Cr | 126                    | 51                     |
| Pd_{3}Co | 155                    | 160                    |
| Pd_{3}Ni | 61                     | 62                     |
| Pt_{3}Cr | −68                    | −139                   |
| Pt_{3}Co | 31                     | 42                     |
previous calculation \([14]\) of 2.6 \(\mu_B\) and with the experimental value \([15]\) of 2.5 \(\mu_B\).

(iii) In the NM calculations, Pd\(_3\)V and Pd\(_3\)Cr have large DOS peaks at \(E_F\) in the \(L1_2\) structure, and are concomitantly less stable in this structure than in the low \(N(E_F)\) \(DO_{22}\) structure. However, as spin-polarization is introduced, the large DOS peak of the \(L1_2\) structure splits, so that \(E_F\) now resides in a low DOS region. This leads, simultaneously, to the formation of larger magnetic moments on V and Cr in the \(L1_2\) structure relative to the \(DO_{22}\) structure. This selective magnetization thus lowers the energy of the \(L1_2\) structure more significantly than in the \(DO_{22}\) structure [Fig. 3(b)].

(iv) Table II shows that the more stable of the two structures generally (and weakly) relates with a smaller value of the ferromagnetic DOS at the Fermi level \(N_{FM}(E_F)\). Thus, the trend of total energy stability with \(N(E_F)\) does exist, but for the spin-polarized quantities.

(v) The magnetic stabilization energy \(\Delta M\), reverses the relative stability predicted by NM calculations in several cases: spin-polarization stabilizes the experimentally observed \([2]\) \(L1_2\) structure of Pd\(_3\)Cr, Pd\(_3\)Mn, and Pt\(_3\)Cr (nearly so for Pd\(_3\)Fe) over the \(DO_{22}\) structure, while for Pd\(_3\)Co, spin-polarization makes the \(DO_{22}\) structure more stable. The reversal of stability for Pd\(_3\)Co can not be observed experimentally, since the calculated \(\Delta H\) [Eq. 1] and Table I is positive, so Pd\(_3\)Co (and similarly, Pd\(_3\)Ni) is predicted to phase separate rather than to order, in accord with the observed phase-separation behaviors for Pd-Co and Pd-Ni. \([2]\)

(vi) Spin-polarization can stabilize ordering over phase-separation: \([1]\) We find that in a NM description Pt\(_3\)Co has \(\Delta H_{NM} > 0\) so it is predicted to phase separate, but that a strong spin-polarization effect stabilizes the ordered \(L1_2\) structure, leading to \(\Delta H_{FM} < 0\) in agreement with the observed ordering behavior. \([2]\) Similarly, spin-polarization stabilizes the experimentally observed \([2]\) \(L1_2\) structure of Pd\(_3\)Cr (its magnetic behavior has, however, not been experimentally examined). Hence, spin-polarization not only reverses the stability of the \(L1_2\) and \(DO_{22}\) structures for many compounds, but it also stabilizes an ordered (\(L1_2\)) structure over phase-separation for Pd\(_3\)Cr and Pt\(_3\)Co.

(vii) Interestingly, the \(\Delta H\) for Pt\(_3\)Cr are negative in both the NM and FM cases, but the spin-polarization effect gives a larger stability to the \(L1_2\) structure (observed experimentally). \([1]\) One also notices that the \(\Delta H\) are lower in the Pt alloys than in the corresponding Pd alloys. The increased stability in Pt alloys has been addressed previously in Ref. \([15]\).

In summary, we have shown that a theoretically unstable non-magnetic structures which involve magnetic atoms and possesses large \(N(E_F)\), may be stabilized by splitting the near \(E_F\) peak in the DOS and forming a local magnetic moment with a concomitant lowering of \(N(E_F)\) and the total energy. Therefore, theoretical stud-

ies of the stability of compounds with a large value of a NM \(N(E_F)\) should be carefully tested for magnetic ordering which can often change the predictions of the ground state crystal structure.

We thank Professor Alan Ardell for pointing out the fact that Pd\(_3\)Cr orders in the \(L1_2\) structure. ZWL and BMK acknowledge the support by the University Research Funds of the University of California at Davis and San Diego Supercomputer Center for computer time. AZ acknowledges the DOE, the office of energy research, basic energy sciences, division of materials science for support under the contract No. DE-AC36-83CH10093.

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