

Predicted Suppression of the Superconducting Transition of New High-Pressure Yttrium Phases with Increasing Pressure from First-Principles Calculations

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Structure searches for new high-pressure phases of Y metal have been performed by using evolutionary algorithms in conjunction with a first-principles, pseudopotential plane-wave method based on density functional theory. The *oF16-Fddd* and *hP3-P3₁21* phases are predicted to be energetically favorable at pressures over 97 GPa. These two phases are shown to be dynamically stable by computing their phonon dispersions. We thus propose that *oF16-Fddd* and *hP3-P3₁21* are the most probable crystal structures Y may take in the 97–206 GPa range. The superconducting critical temperatures (T_c) of the new phases are estimated using the Allen-Dynes formula. The T_c is predicted to decrease with increasing pressure over about 100 GPa, in sharp contrast to its observed monotonic increase under lower pressure. The electronic origins of the stabilities of the proposed high-pressure phases have also been investigated.

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Experimental determination of the crystal structures of materials becomes difficult under extremely high pressure. Fortunately, recent developments in the methods for theoretical predictions of crystal structures provide an effective way to search for novel high-pressure phases. A number of successful applications of these methods which include the *ab initio* random structure searching [1–6] and evolutionary approaches [7–11] have been reported recently. As an example, sodium was predicted to take the *hP4* structure under high pressure by Ma *et al.* [7] who employed an evolutionary approach. The *hP4* phase has then been found to be responsible for the transformation of Na into an optically transparent phase at about 200 GPa. The successful applications of the structure searching approaches show their capabilities of predicting complex configurations given only the compositions of the system.

A large number of elements and compounds undergo superconducting transitions under pressure, in particular, the critical temperatures T_c may increase with hydrostatic pressures. Therefore, the predictions of the crystal structures of high-pressure phases become invaluable in searching for high T_c superconductors. Yttrium has recently been reported to exhibit superconductivity at 17 and 20 K at pressures of 89 and 115 GPa, respectively, which qualifies it (together with Li [12]) as the highest T_c elemental superconductor [13–15].

Within the framework of routine density functional theory (DFT), the current authors investigated the structural phase transitions of Y with pressure up to 300 GPa in a recent publication [16]. The structural transition pressures with regard to, hexagonal close-packed (hcp) → samarium-type (Sm-type) → double hexagonal close-packed (dhcp) → distorted face-centered cubic (dfcc), was estimated to be 0, 7 and 51 GPa, respectively. In addition, a new phase *hP3-P6₂22* (the Pearson symbol

and space group), which had never been observed experimentally, was predicted to be energetically preferable over about 100 GPa. However, the *hP3-P6₂22* phase is unlikely to be observed at a pressure lower than 206 GPa due to the existence of imaginary phonon frequencies. Large enthalpy differences between the *hP3-P6₂22* and dfcc phases in the pressure range of 100–206 GPa imply the possible existence of yet unknown phases.

Since the crystal structure of Y in the 100–206 GPa range is of great importance for understanding its extraordinary superconducting behaviors, in this Letter, we perform theoretical searches for the new phases of Y at 140 GPa using evolutionary algorithms (EAs) and a first-principles method based on DFT. A group of energetically preferable crystal structures found in the evolutionary searches are then investigated in detail and compared with the experimentally observed phases with pressure up to 300 GPa. It is found that, considering the accuracy of DFT calculations, the *oF16-Fddd*, *hP3-P3₁21* and *hP3-P6₂22* phases become indistinguishable in enthalpy over about 100 GPa. Moreover, contrary to the *hP3-P6₂22* phase showing imaginary phonon frequencies at 97 GPa [16], the *oF16-Fddd* and *hP3-P3₁21* phases are dynamically stable, which makes them the most probable crystal structures Y may take over about 100 GPa. Based on our newly proposed crystal structures, the Eliashberg functions $\alpha^2F(\omega)$ and the electron-phonon (*e*-ph) coupling constants λ are calculated to analyze the superconducting features of Y under high pressure. The projected band structures, density of states (DOS), and charge density differences of the *oF16-Fddd* and *hP3-P3₁21* phases at 0 and 97 GPa are then compared to investigate the electronic origins of their stabilities at high pressure.

We have performed evolutionary searches for the energetically preferable crystal structures at $T = 0$ K and

$P = 140$ GPa using USPEX [17–19] in conjunction with VASP [20,21], which enable us to search for the global minimum of the enthalpy. Unit cells with 8, 10, and 12 atoms are used for the EA structure searches. For local crystal structure relaxations, projector augmented wave pseudopotentials [22] are applied, and the generalized gradient approximation [23] is adopted to describe the electronic exchange-correlation potential. The semicore $4s$ and $4p$ orbitals of Y have been treated as valence states. We apply a plane-wave energy cutoff of 480 eV and dense ($2\pi \times 0.025 \text{ \AA}^{-1}$ resolution) Monkhorst-Pack k meshes [24] to ensure that the enthalpy differences converge to typically 1–2 meV/atom. Cell shapes and atomic coordinates are relaxed with the constraints of constant volumes before the enthalpies are calculated as functions of pressure. Phonon dispersions and e -ph couplings are computed within the density functional perturbation theory (DFPT) using the QUANTUM-ESPRESSO package [25,26].

The unit cells of the energetically preferable crystal structures produced by EA structure searches at 140 GPa are shown in the top panel of Fig. 1. The $oC8-C222_1$, $oF8-Fddd$, $oF16-Fddd$, and $hP3-P3_121$ structures have four, two, four, and three atoms in their primitive cells, respectively. The enthalpies of Y in these four crystal

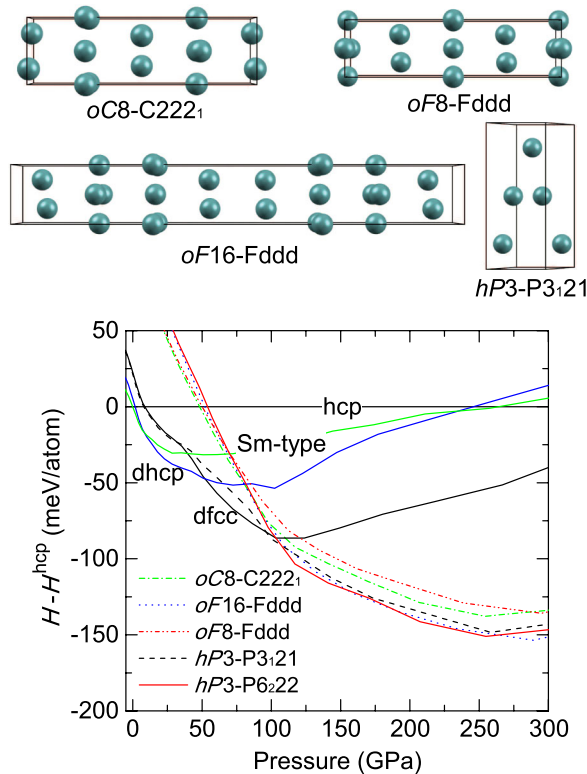


FIG. 1 (color online). Top: The unit cells of the energetically preferable phases generated by first-principles evolutionary searches at 140 GPa. Bottom: The enthalpy differences (relative to hcp) of Y in competing crystal structures as functions of pressure.

structures are computed as functions of pressure and compared with the experimentally observed phases as well as the theoretically predicted $hP3-P6_222$ [16]. It is worth noting that both of the $dfcc$ and $hP3-P3_121$ phases transform to fcc during structural relaxations and show identical enthalpies at pressures below about 35 GPa. In addition, the enthalpies of the $oF16-Fddd$, $hP3-P3_121$, and $hP3-P6_222$ phases become indistinguishable within the accuracy of typical DFT calculations and the lowest among all the competing phases at pressures above 97 GPa. In our previous publication [16], we pointed out that the $hP3-P6_222$ phase is dynamically unstable below about 206 GPa due to the imaginary phonon frequencies; therefore, $oF16-Fddd$ and $hP3-P3_121$ produced by EA structure searches become the candidate crystal structures of Y in the 97–206 GPa pressure range. Nevertheless, the $oC8-C222_1$ and $oF8-Fddd$ phases are unlikely to be observed experimentally due to their relatively high enthalpies throughout the whole pressure range that we have considered.

The predicted lattice constants and atomic coordinates of the $oF16-Fddd$, $hP3-P3_121$, and $hP3-P6_222$ phases at 97 GPa are summarized in Table I. Not surprisingly, the lattice constants of the $hP3-P3_121$ and $hP3-P6_222$ phases are very close to each other due to the similar atomic arrangements in their unit cells. It is also found that $hP3-P3_121$ transforms to $hP3-P6_222$ with the atomic coordinates taking (0.50, 0.50, 0.83) during structural relaxations at pressures above approximately 200 GPa. Under the perturbation of the imaginary phonon mode shown in our previous publication [16], $hP3-P6_222$ relaxes to $hP3-P3_121$ (or its enantiomorph $hP3-P3_2121$) below about 200 GPa.

To be observed experimentally under high pressure, the $oF16-Fddd$ and $hP3-P3_121$ phases have to be dynamically stable. To clarify this issue, phonon dispersions along the high-symmetry directions of the Brillouin zones of these two phases at 97 GPa are computed and shown in the top panels of Fig. 2. Contrary to the $hP3-P6_222$ phase which exhibits imaginary phonon frequencies throughout the Brillouin zone at 97 GPa (see Fig. 5 of Ref. [16]), no soft modes are found for the $oF16-Fddd$ and $hP3-P3_121$ phases. Thus, we propose that $oF16-Fddd$ and $hP3-P3_121$ are the most probable crystal structures Y may take under pressures above approximately 100 GPa, where the

TABLE I. Predicted lattice constants and atomic coordinates, as referred to the conventional unit cells, of the $oF16-Fddd$, $hP3-P3_121$ and $hP3-P6_222$ phases at 97 GPa.

Structure	a (Å)	b	c	Fractional coordinate
$oF16-Fddd$	4.81	2.83	17.70	(0.25, 0.25, 0.56)
$hP3-P3_121$	2.79	2.79	6.71	(0.56, 0.44, 0.83)
$hP3-P6_222$	2.81	2.81	6.60	(0.50, 0.50, 0.83)

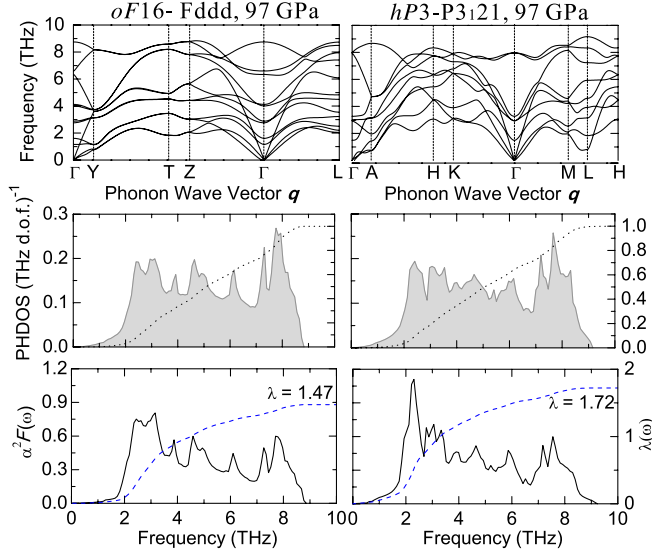


FIG. 2 (color online). The phonon dispersions (top), PHDOS (middle), and Eliashberg functions $\alpha^2F(\omega)$ (bottom) of the $oF16-Fddd$ and $hP3-P3_{121}$ phases at 97 GPa. The integrals of PHDOS (dotted lines) and the e -ph coupling constants λ (dashed lines) are referenced to the right axes.

experimentally observed dfcc phase becomes energetically unfavorable.

Hamlin *et al.* have recently reported that the superconducting critical temperature T_c of Y increased monotonically with pressure and reached a record value of 20 K at 115 GPa [13]. Based on our newly proposed high-pressure phases of Y, we are now able to theoretically estimate the T_c up to a higher pressure.

The phonon density of states (PHDOS), Eliashberg functions $\alpha^2F(\omega)$, and e -ph coupling constants λ of the $oF16-Fddd$ and $hP3-P3_{121}$ phases at 97 GPa are computed using fine k and q meshes (see the middle and bottom panels of Fig. 2). The Eliashberg functions integrate to large λ of 1.47 and 1.72 for the $oF16-Fddd$ and $hP3-P3_{121}$ phases, respectively, with over half of the values contributed from the phonon modes in the range of 2–4 THz. By assigning μ^* with a typical value in the 0.10–0.15 range, we have evaluated T_c using Allen-Dynes formula [27,28]. Both of the $oF16-Fddd$ and $hP3-P3_{121}$ phases are estimated to exhibit T_c in the range of 16–19 K at 97 GPa.

By using the same scheme, the T_c of different high-pressure phases of Y is calculated and compared with available experimental values in Fig. 3. For the dhcp and dfcc phases, the theoretical T_c increases with pressure, in good agreement with experimental measurements. In sharp contrast to the behavior of T_c against pressures below 100 GPa, the T_c of the newly predicted phases ($oF16-Fddd$ and $hP3-P3_{121}$) at higher pressure decreases with pressure. In other words, a higher T_c may not be observed in experiments by further increasing the pressure

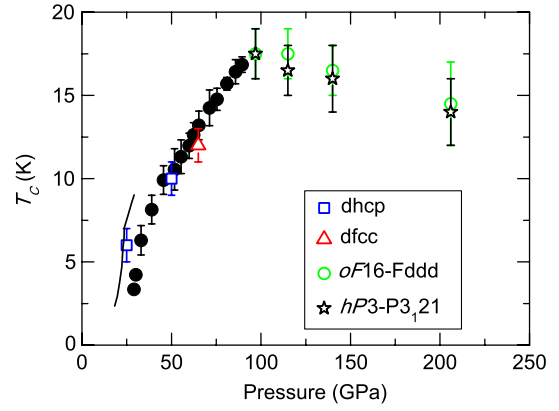


FIG. 3 (color online). The theoretically estimated superconducting critical temperatures T_c (open symbols) of different ground-state structures of Y under high pressures. The solid circles and line denote the experimental values (see Fig. 2 of Ref. [13]).

beyond about 100 GPa. The value of T_c is found to be closely related to the e -ph couplings in the systems; as for the $oF16-Fddd$ and $hP3-P3_{121}$ phases, we find that their λ decreases significantly with pressure.

To investigate the electronic origins of $oF16-Fddd$ and $hP3-P3_{121}$ becoming the energetically preferable phases at pressures above 97 GPa, we compare their projected band structures and DOS at 0 and 97 GPa in Fig. 4. It is noticed that the s electrons occupy the low-energy levels at 0 GPa, while the d electron energy levels dramatically decrease at 97 GPa, which significantly lowers the total energies and results in the transfer of s to d electrons. Similar s to d electron transfer was also concluded from experiments [29,30] and canonical tight-binding calculations [31] for rare earth elements. Therefore, the shift of the d electron energy levels and the related s to d electron transfer are believed to be important for the static stabilities of the $oF16-Fddd$ and $hP3-P3_{121}$ phases with increasing pressure. By comparing the DOS at 0 and 97 GPa, it is obvious that the electronic states located at low-energy levels, especially those between -4 to -2 eV, increase significantly at 97 GPa. In the meantime, the DOS at Fermi level decrease, respectively, from 2.18 and 1.53 (eV atom) $^{-1}$ at 0 GPa to 0.90 and 0.67 (eV atom) $^{-1}$ at 97 GPa for the $oF16-Fddd$ and $hP3-P3_{121}$ phases. These considerable changes in DOS are believed to contribute greatly to the phase stabilities of $oF16-Fddd$ and $hP3-P3_{121}$ under high pressure.

Charge density differences on the (010) atomic plane of $oF16-Fddd$ and the $(\bar{2}03)$ atomic plane of $hP3-P3_{121}$ at 0 and 97 GPa are compared in Fig. 5 in order to investigate the influences of pressure on the chemical bonding of the systems. It is obvious that electrons tend to move away from the Y1–Y2 bond and accumulate between Y3–Y4 for the $oF16-Fddd$ phase at 97 GPa, where the bond lengths of Y1–Y2 and Y3–Y4 are, respectively, 2.63 and 3.27 Å. For the $hP3-P3_{121}$ phase at 97 GPa, the electrons move

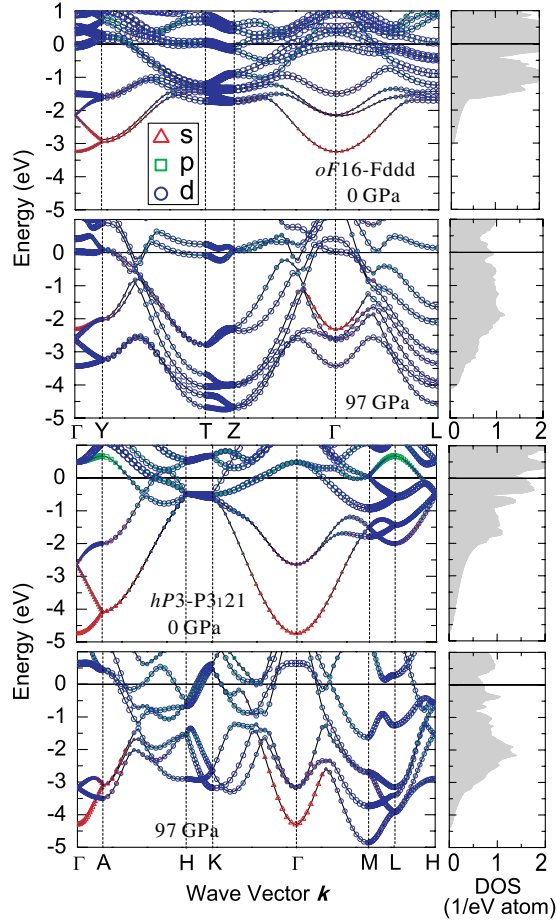


FIG. 4 (color online). The electronic band structures and DOS of the *oF16-Fddd* and *hP3-P3₁₂₁* phases under pressures of 0 and 97 GPa. Energy is relative to the Fermi level, which is located at 0 eV. The projected *s*, *p*, and *d* electron characters are denoted by discrete symbols.

away from the Y1–Y2 bond and accumulate between Y1–Y4, nonetheless, no obvious changes in the charge densities are observed for the Y1–Y3 bond. The bond lengths of Y1–Y2, Y1–Y3, and Y1–Y4 are, respectively, 2.65, 2.79, and 3.10 Å for the *hP3-P3₁₂₁* phase at 97 GPa. Therefore, the observed accumulations of electrons to the interstitial sites of the lattices of *oF16-Fddd* and *hP3-P3₁₂₁* may account for their stabilities at high pressure. Pickard and Needs have proposed that *sp*-bonded materials could be commonly described by a two-component model consisting of positive ions and interstitial electron *blobs* at multiterapascal pressure [5]. In this Letter, we find that *d*-bonded transition metal Y already exhibits a tendency of similar behavior at a pressure of 97 GPa; thus, the two-component model proposed primarily for *sp*-bonded materials may be valid for more general substances.

In summary, we have employed EAs in conjunction with DFT to perform structure searches for new high-pressure phases of Y metal. The *oF16-Fddd* and *hP3-P3₁₂₁* phases

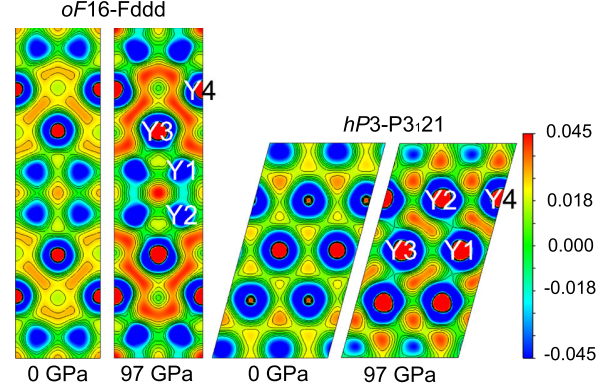


FIG. 5 (color online). The charge density differences (in \AA^{-3} , plotted with VESTA [32]) on the (010) atomic plane of *oF16-Fddd* and the $(\bar{2}03)$ atomic plane of *hP3-P3₁₂₁* at 0 and 97 GPa.

are predicted to be energetically and dynamically stable, and are proposed to be the most probable crystal structures which Y may take in the 97–206 GPa range. We have successfully reproduced the experimentally measured T_c of Y below about 100 GPa. More importantly, the T_c is predicted to decrease under higher pressure, in sharp contrast to its observed behavior below about 100 GPa (it increases monotonically with pressure). The decrease in T_c is found to be closely related to the *e*-ph couplings in the systems. By comparing the projected band structures and DOS of the *oF16-Fddd* and *hP3-P3₁₂₁* phases at 0 and 97 GPa, we find that the shifts of *d* electron states to low-energy levels and the significant decreases in the DOS at Fermi levels at high pressure contribute to their phase stabilities. In addition, the accumulations of electrons into the interstitial sites of the lattices also play an important role under high pressure.

Since Y is one of the highest T_c elemental superconductors under high pressure, our proposed new phases and their unexpected behaviors of T_c above 97 GPa may stimulate future experimental and theoretical investigations for a better understanding of its superconducting features.

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