Comparative study of high-\(T_c\) superconductivity in \(\text{H}_3\text{S}\) and \(\text{H}_3\text{P}\)

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(Dated: July 5, 2016)

PACS numbers: 71.15.Mb, 71.20.-b, 74.20.Fg, 74.62.Bf

I. INTRODUCTION

Many materials have been proposed theoretically as conventional phonon-mediated superconductors having a high superconducting transition temperature \(T_c\). Based on the BCS theory, materials with light masses and strong bonds are promising candidates for high-\(T_c\) superconductors because \(T_c\) is scaled by the inverse square root of the atomic mass. Therefore, theoretical studies have been intensively performed focusing on the crystal structures of these two materials are similar, there are notable changes in the phonon spectra and electron-phonon coupling. The low-frequency bond-bending modes are softened in \(\text{H}_3\text{P}\) and their coupling to the electrons at the Fermi surface is enhanced relative to \(\text{H}_3\text{S}\). Nevertheless, coupling to the high-frequency modes is reduced so the resulting calculated superconducting transition temperature is reduced from \(\sim 166\,\text{K}\) in \(\text{H}_3\text{S}\) to \(\sim 76\,\text{K}\) in \(\text{H}_3\text{P}\).

II. METHODS

The following methods are used to perform the calculations of the electronic structures, phonon properties, and superconducting properties. For the electronic structures, our calculations are based on \textit{ab-initio} norm-conserving pseudopotentials and the Perdew-Burke-Ernzerhof functional as implemented in the SIESTA codes. Phonon frequencies are computed using density-functional perturbation theory implemented in Quantum-ESPRESSO package. Finally, EPC and Eliashberg spectral functions are obtained via the Wannier90 and EPW packages.

For the calculation using SIESTA, electronic wavefunctions are expanded with pseudoatomic orbitals (double-\(\zeta\) polarization) and a charge density cutoff of 800 Ry is used. We sample the Brillouin zone on a uniform \(16\times16\times16\) k-point mesh. For the calculation with Quantum-ESPRESSO, a plane-wave basis up to 160 Ry and a \(32\times32\times32\) k mesh size are employed.

Phonon frequencies \(\omega_{\mathbf{q}\nu}\) and EPC parameters \(\lambda_{\mathbf{q}\nu}\) are computed on a coarse mesh \((8\times8\times8)\) of reciprocal space. Next, interpolation techniques based on maximally localized Wannier functions are used to interpolate EPC parameters on a fine grid \((36\times36\times36)\).

The Eliashberg spectral function \(\alpha^2 F(\omega)\) is computed by integrating the interpolated phonon frequencies \(\omega_{\mathbf{q}\nu}\) and the EPC \(\lambda_{\mathbf{q}\nu}\) over the Brillouin zone,

\[
\alpha^2 F(\omega) = \frac{1}{2} \sum_{\mathbf{q}\nu} \omega_{\mathbf{q}\nu} \lambda_{\mathbf{q}\nu} \delta(\omega - \omega_{\mathbf{q}\nu}).
\]

Here the \(w_\mathbf{q}\) is the Brillouin zone weight associated with the phonon wavevectors \(\mathbf{q}\). The total EPC \(\lambda\) is calculated as the Brillouin zone average of the mode-resolved coupling strengths \(\lambda_{\mathbf{q}\nu}\):

\[
\lambda = \sum_{\mathbf{q}\nu} w_\mathbf{q} \lambda_{\mathbf{q}\nu} = 2 \int_0^{\infty} d\omega \, \alpha^2 F(\omega)/\omega.
\]
FIG. 1. The $Im\overline{3}m$ crystal structure assumed for $H_3S$ and $H_3P$. The large sphere (orange) is S or P, and the small sphere (white) is H.

III. ELECTRONIC STRUCTURE

Here we discuss the electronic structure of $H_3S$ and $H_3P$. In all of our calculations we set the conventional lattice parameter as 3 Å. With this lattice parameter, the calculated pressures of both materials are 220 GPa.

The overall shapes of the band structures are similar for both materials [Figs. 2(a) and (c)]. Because phosphorus has one less valence electron than sulfur, the Fermi level ($E_F$) is shifted down in $H_3P$. With the shift, $E_F$ of $H_3P$ is placed near a different peak position in the density of states (DOS). For $H_3S$, the DOS at $E_F$ is calculated to be 0.45 states eV$^{-1}$ f.u.$^{-1}$. A similar value (0.50 states eV$^{-1}$ f.u.$^{-1}$) for the DOS is found in the case of $H_3P$.

Figure 2 compares the orbital contributions to the band structure and DOS in $H_3S$ and $H_3P$. In both materials, the DOS at $E_F$ comes dominantly from 3$p$ orbitals of sulfur or phosphorus. The portion of 3$p$ orbitals is twice as large as the portion of hydrogen orbitals. The Fermi surfaces originated from hydrogen orbitals are almost same in both case, forming small hole pockets centered at $\Gamma$-point.

IV. PHONON PROPERTIES

In this section we discuss the differences of the phonon properties between $H_3S$ and $H_3P$. When the sulfur is changed to phosphorus, the characteristics of the phonon spectra differ significantly along $\Gamma$–H and H–N high-symmetry lines [Fig. 3]. The hydrogen–phosphorus bond-bending modes become softer and three unstable phonon modes appear at the $H$ high-symmetry point. Therefore we expect that in the doubled unit cell these unstable modes would be stabilized. We exclude these negative phonon modes when calculating $\alpha^2F$ so that we can make an reliable comparison with $H_3S$. The structural instability of body-centered cubic $H_3P$ is also reported by previous theoretical structural studies.27,28

Next we discuss the strength of the EPC for the two cases. In $H_3S$, phonon modes of 150–200 meV frequencies (which are $H$–S bond-stretching modes) are strongly coupled to electrons at the Fermi surface. In $H_3P$, however, low-frequency modes ($< 50$ meV) are more relevant. These modes originate from softened $H$–$P$ bond-bending motion.

To give a more quantitative discussion about the relevant energy scales of the phonons, we calculate the EPC-weighted average of the phonon frequencies,

$$\omega_{in} = \exp \left\{ \frac{2}{\lambda} \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega} \ln \omega \right\}. \quad (3)$$

The value of $\omega_{in}$ is 1580 K (136 meV) for the $H_3S$ and 610 K (53 meV) for the $H_3P$. Therefore $\omega_{in}$ is more than twice as large in $H_3S$ relative to $H_3P$. 
V. SUPERCONDUCTING PROPERTIES

The total EPC $\lambda$ equals 1.38 in H$_3$S, whereas it reaches 1.66 in H$_3$P. The Eliashberg phonon spectral functions of H$_3$S and H$_3$P are quite different. The EPC in H$_3$S is dominated by the phonon modes at the zone center $\Gamma$ point. In H$_3$P, however, we observed an overall contribution of different modes to $\lambda$ along $\Gamma$–$H$–$N$ directions as shown in Fig. 3.

Here we discuss why there is a large difference in the EPC between H$_3$S and H$_3$P. First, we consider the difference in DOS. Since $\lambda$ is roughly proportional to the DOS at $E_F$, the EPC could be enhanced by the large DOS. However, in our case, there is no sufficient change in DOS to reproduce the large enhancement in EPC for H$_3$P. Another point is the coupling strength between the electrons and the low-frequency hydrogen vibration. There is no significant enhancement in the electron-phonon matrix elements which is proportional to $\omega_{\mathbf{q},\mathbf{q}'}$. But, the dominant modes to EPC appear at low frequencies in H$_3$P [Fig. 3]. This change causes the enhancement of the EPC $\lambda$ value.

Finally, we estimate the superconducting transition temperature $T_c$ using the McMillan equation

$$T_c = \frac{\omega_{\text{in}}}{1.20} \exp \left\{ -\frac{1.04 (1 + \lambda)}{\lambda - \mu^* (1 + 0.62 \lambda)} \right\}.$$  (4)

Here $\mu^*$ is the Coulomb repulsion parameter. For commonly used $\mu^* = 0.1$ we estimate $T_c = 166$ K for H$_3$S and 76 K for H$_3$P. The exact value of $\mu^*$ here is not that important since even with $\mu^* = 0$ we get very similar $T_c$ (219 and 96 K).

The value of $\lambda$ we obtained for H$_3$S and H$_3$P is near the limit of applicability of the McMillan equation. However, we find that the Kresin–Barbee–Cohen model, which is applicable for large $\lambda$, gives similar estimates for $T_c$.

Although H$_3$P has a higher $\lambda$ value than H$_3$S, the estimated $T_c$ is about half of that in H$_3$S. This agrees well with the experimentally obtained $T_c$ of ~200 K in H$_3$S and ~100 K in H$_3$P. We expect that the deviation here from experiment might occur because we ignored unstable phonon modes in our calculation, so softening might be overestimated for H$_3$P in the low-frequency regime.

VI. CONCLUSION

With the assumption of the same body-centered cubic structure and lattice parameter, we compare the electronic, phonon, and superconducting properties of H$_3$S and H$_3$P. The results of electronic structures show no significant difference, except for a slight change in the Fermi level due to the different number of valence electrons. However, there are notable changes in phonon spectrum and electron-phonon coupling properties. First, there exists phonon softening in low-frequency bond-bending modes, and the coupling of these modes to electrons near the Fermi surface is enhanced. As the dominant frequency regime changes from high to low frequency, the superconducting transition temperature is reduced from ~166 K in H$_3$S to ~76 K in H$_3$P.
ACKNOWLEDGEMENTS

This work was supported by National Science Foundation Grant No. DMR15-1508412 (electronic structure calculation) and by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, U.S. Department of Energy under Contract No. DE-AC02-05CH11231, within the Theory Program (phonon and superconducting properties calculations). Computational resources have been provided by the DOE at Lawrence Berkeley National Laboratory’s NERSC facility.

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