Cubic Ca$_3$I$_3$P with ideal charge-two triple point

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A recent study reported the enhancement of thermoelectric response due to the presence of triple point phonons [Phys. Rev. Mater 2, 114204 (2018)]. Because the topological triple point phonons field is still at its early stage, it is necessary to search for realistic materials with ideal triple point phonons. In this work, we show that cubic Ca$_3$I$_3$P is an excellent material to host the ideal charge-two triple points at high-symmetry points $\Gamma$ and H. Because the charge-two triple points have a topological charge of $|C| = 2$, two arc-shaped surface states emanating from the projections of each charge-two triple nodal point can be found in cubic Ca$_3$I$_3$P. It is hoped that the ideal charge-two triple point phonons and the clean phononic arc-shaped surface states in Ca$_3$I$_3$P can be experimentally confirmed shortly.

KEYWORDS

triple point, topological phonons, phonon band crossings, topological charge, arc-shaped surface states

Introduction

The study of topological behaviors in condensed matter systems [1–10] has generated much interest in solid-state physics over the past 10 years. Emergent low-energy quasiparticles in solid states, derived from the intrinsic topological order of the crystalline, can serve as exotic analogs of the elementary particles in high-energy physics and thus serve as a valuable platform to examine the related fundamental physics. Significant accomplishments have been made thanks to ongoing work and development, mainly since the topological band theory was established. Beyond the conventional Weyl, Dirac, and Majorana particles under the Poincare symmetry, many more unconventional topological quasiparticles [11–20] have been predicted thus far. In solid states, these quasiparticles can exhibit a variety of topological charges, dispersion types, and pseudospin structures.

The current study of crystal topology has even been further extended to bosons, including phonons, photons, and magnons. Phonons [21–40] can be a perfect platform for realizing these quasiparticles owing to their unique device applications and the advantages of whole frequency range observation. For example, in the phonon dispersion of three-dimensional-SiO$_2$, Wang et al. [40] proposed a topological triangular Weyl complex made up of one double Weyl point and two single Weyl points. In realistic three-dimensional materials with space group numbers 195–199, and 207–214, Liu et al. reported charge-four Weyl point phonons. Xie et al. [24] reported that sixfold degenerate nodal-point phonons could appear in three-dimensional materials Ca$_3$N$_4$, Sc$_3$C$_6$, Y$_3$Sb$_3$.
and K₈Si₄₆. Chen et al. [39] systematically studied three-dimensional Dirac phonons in 2021. As potential candidates for materials with Dirac point phonons, some realistic three-dimensional materials are also put forth in their work. In 2022, Ding et al. [32] reported that three-dimensional BaZnO₂ has a type-III charge-two Weyl point phonon and double-helicoid phonon surface states. Experimentally, inelastic x-ray scattering was used to identify the double Weyl points in three-dimensional FeSi [36, 38], which was a significant driving force for the field.

According to a recent study by Singh et al. [41], the presence of triple point phonons enhances the thermoelectric response. However, only a handful of candidate materials are proposed to host triple-point phonons. At the very least, the material should meet the following criteria to qualify as a good candidate for triple nodal point phonons. First, there must be no nearby extraneous phonon bands at a particular frequency, as such a situation may make it more challenging to interpret the measured properties. Second, candidate materials with triple nodal point phonons should have more evident arc-shaped surface modes (i.e., not covered by the bulk phonon modes). It is still urgently necessary to search for realistic material systems with ideal triple nodal point phonons due to these limitations on potential materials.
In this work, we selected a realistic material, cubic Ca$_3$I$_3$P with space group 214 [42], to be the ideal material candidate with two charge-two triple nodal points at points $\Gamma$ and H. The clean and visible double arc-shaped surface states can be found, which benefits the experimental detection.

Computational methods

We perform the first-principle calculations based on the density functional theory (DFT) [43]. The generalized gradient approximation (GGA) [44] with Perdew–Burke–Ernzerhof (PBE) [45] realization was adopted for the exchanged correlation potential. The phonon spectra of cubic Ca$_3$I$_3$P is calculated by using the Phonopy code. The pre-process and post-process were performed in the PHONOPY package using density functional perturbation theory (DFPT) [46]. The cutoff energy for the plane wave was 600 eV, and the Brillouin zone is sampled using converged 5 $\times$ 5 $\times$ 5 $\Gamma$-centered $k$-mesh grids. To study the topological properties of nontrivial band crossings in the phonon spectrum, we calculate its corresponding surface states and constant frequency slices using the WANNIERTOOLS package [47]. In this work, the phononic surface spectrums were simulated by the following steps: 1) by calculating the phonon dispersion of a slab system; 2) First, we used the phonopyTB tool, installed in the root folder of WannierTools [47], to generate the phononic tight-binding Hamiltonian with the FORCE–CONSTANTS. Then, we used the iterative Green’s function method to calculate the surface states of phonons in the software package WannierTools [47].

Results and discussion

The crystal structure of cubic Ca$_3$I$_3$P with space group I4$_1$32 is shown in Figure 1A. Ca$_3$I$_3$P is a colorless insulator [48], as expected from the closed-shell electronic configuration of (Ca$^{2+}$)$_3$(I$^-$)$_3$P$^-$$. The obtained lattice constants for cubic Ca$_3$I$_3$P are a = b = c = 10.779 Å, agreeing well with the experimental lattice constants a = b = c = 10.665 Å [42]. The Ca, I, and P atoms locate at 48i (−0.26853, −0.98147, 0.03706), 24i (0.74736, −0.75000, −0.24736), 8f (−0.25 −0.75000 0.25000) Wyckoff positions, respectively. Ca$^{2+}$ is bonded to two equivalent P$^-$ and four equivalent I$^-$ atoms to form a mixture of edge and corner-sharing CaP$_2$I$_4$ octahedra. P$^-$ is bonded to six equivalent Ca$^{2+}$ atoms to form edge-sharing PCa$_6$ octahedra. I$^-$ is bonded in a distorted rectangular see-saw-like geometry to four equivalent Ca$^{2+}$ atoms.

The phonon dispersion for cubic Ca$_3$I$_3$P along G -P-H- G -N-H-N-P (see Figure 1B) is exhibited in Figure 2A. At first glance, the cubic Ca$_3$I$_3$P is dynamically stable due to the absence of imaginary frequencies. We only focus on the R1 region, where two obvious triple nodal points appear at high-symmetry points. The enlarged figure of the phonon bands in R1 regions is exhibited in Figure 2B. From Figure 2B, two charge-two triple nodal points with a topological charge $|C| = 2$ can be found at high-symmetry points $\Gamma$ and H. Moreover, one finds that the phonon bands from the two charge-two triple nodal points are pretty clean. The three-dimensional plots of the phonon bands around these two charge-two triple nodal points are shown in Figures 3A,B. Obviously, the charge-two triple nodal point (C-2 TP) is a zero-dimensional threefold band degeneracy and features a linear energy splitting along any direction in momentum space. Note that the charge-two triple nodal point can only appear at a high-symmetry point in three-dimensional BZ.

Nontrivial surface states can characterize these charge-two triple nodal points. To obtain the surface states for cubic Ca$_3$I$_3$P, a surface slab model has been constructed along the (010) surface. The calculated phononic local density of the surface states for cubic Ca$_3$I$_3$P is shown in Figure 4B, and the corresponding surface path can be referred to in Figure 4A. The surface spectra of cubic Ca$_3$I$_3$P are very clean and arise from the projections of the two charge-two triple nodal points.
Interestingly, the phononic arc state around the projected point of the nodal point shows chirality-dependent properties [49]. Because the charge-two triple nodal point has a topological charge of $|\chi| = 2$, two phononic arcs would be observed in cubic Ca$_3$I$_3$P. Surface states on the (010) surface at 3.60 THz and 3.45 THz are shown in Figure 5A and Figure 5B, respectively. Indeed, one could observe that two arcs emanate from the projections of the two charge-two triple nodal points, as shown in Figure 5.

Examining the distinctive physical characteristics of the topological phonon states will be a crucial objective of upcoming research. Inelastic x-ray scattering has been used in topological phonon experiments thus far to visualize the topological band degeneracy. We need to look for other measurable effects from the topological phonons and to propose sound material systems. In order to detect these effects experimentally, new methods must be developed, precisely ways to separate the signal from topological modes. In an experiment, the surface phonon modes can be verified by high-resolution electron energy loss spectroscopy, helium-atom scattering, or THz spectroscopy.

Summary

With the help of first-principle calculations, the phononic charge-two triple nodal points are reported to appear at high-symmetry points in cubic Ca$_3$I$_3$P. In addition, we also studied the phononic surface states and the isofrequency arcs on the (010) surface. Such clean and visible double surface arcs confirm the topological charge of $|\chi| = 2$ for the two triple nodal points in cubic Ca$_3$I$_3$P. Moreover, the nontrivial surface states are long and clean, benefiting the experimental detections soon. Our work not only determines the ideal charge-two triple nodal point states but also confirms the clean and long double phononic surface arcs in cubic Ca$_3$I$_3$P.

Data availability statement

The raw data supporting the conclusion of this article will be made available by the authors, without undue reservation.

Author contributions

YY-investigations and writing.

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