Ideal topological phononic nodal chain in K$_2$O materials class

Y S Chen$^1$, F F Huang$^2$, P Zhou$^{1,*}$, Z S Ma$^3$ and L Z Sun$^{1,*}$

$^1$ Hunan Provincial Key laboratory of Thin Film Materials and Devices, School of Material Sciences and Engineering, Xiangtan University, Xiangtan 411105, People’s Republic of China
$^2$ Key Laboratory of Low-dimensional Materials and Application Technology, School of Material Sciences and Engineering, Xiangtan University, Xiangtan 411105, People’s Republic of China
$^3$ Authors to whom any correspondence should be addressed.
E-mail: zhoupan71234@xtu.edu.cn and lzsun@xtu.edu.cn

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Abstract

Nodal-chain semimetals are characterized by linked nodal rings in Brillouin zone and they have not been reported in the phonon system of atomic crystals yet. Here, based on first-principles calculations and tight-binding model analysis, we propose nearly ideal nodal chains can be realized in the phonon modes of experimentally synthesized ionic crystal K$_2$O materials class. Different from all previous cases, the connection points of the nodal chain in K$_2$O are located at the high symmetry points W and the positions are limited by the symmetries. The nodal rings that forming the nodal chain are symmetrically equivalent and protected by the mirror symmetries. The nontrivial topological properties of nodal chains are validated by the nontrivial Berry phase and surface modes. A general discussion about all symmorphic space groups reveals that, if no more than two inequivalent mirrors exist, $Fm\bar{3}m$ (No. 225) is a unique space group for the appearance of the nodal chain connected at the high symmetry points. Our studies demonstrate that K$_2$O materials class is a wonderful implementable platform to study the nontrivial topological nodal chains in a phonon system.

Topological semimetal states in solid systems provide excellent platforms to study the fermions beyond the elementary particles in high energy physics [1–8]. A typical example among them is the nodal ring, in which the symmetry-protected crossing points form a closed ring in reciprocal space [9–14]. A typical example among topological semimetals is the nodal ring, in which the symmetry-protected crossing points form a closed ring in reciprocal space [9–14]. Based on nodal rings, some of other semimetals, such as nodal chains [15–20], nodal links [21–29], nodal knots [30, 31], are proposed. A nodal chain is composed of a series of tangent nodal rings has been proposed in low-energy electronic states of several materials, including crystal with nonsymmorphic symmetries [15] and HfC [16]. However, the nodal chains of electrons are generally fragile to the spin–orbit coupling (SOC), for example, the nodal chain of HfC will be transformed into Weyl semimetal [16]. Therefore, nodal chains were only observed in the electronic states of TiB$_2$ [17] with negligible SOC and photonic crystal [18] or phononic crystal [19].

Recently, except low-energy electronic states, people find the phonons of a realistic material also provide fertile ground for nontrivial topological semimetals, such as double Weyl points [32, 33], type-II Weyl phonons [34, 35], triangular Weyl complex phonons [36], Weyl nodal straight line [37]. However, as far as we know, a nodal chain in the phonon of materials has not been reported yet. There are two significant advantages that fascinate the detection of nodal chains for phonons. The first one is that their detection is not limited by the occupation of particles since phonons are bosons. Second, an SOC-like term does not exist for phonon states.

In this paper, we first predict the existence of nearly ideal phonon nodal chain in the cubic K$_2$O material class. The polarization correction must be considered for the optical phonons of these materials. As a result, the nodal chain exhibits very small frequency dispersion in reciprocal space. We find a minimal two-band
tight-binding model that can well illustrate the formation and characteristics of the nodal chain. A detailed discussion about the requirement of symmetries to form the nodal chain reveals that \( Fm\bar{3}m \) is the only space group to form the nodal chain connected at high symmetry points in all symmorphic space groups. Considering many of the materials in the K\(_2\)O family have been synthesized in experiments, we expect they can be excellent candidates to study nontrivial phonon nodal chains.

Figure 1(a) presents the conventional cell of K\(_2\)O and it is a typical anti-fluorite material with the space group \( Fm\bar{3}m \) (No. 225). The lattice constant is \( a = 6.348 \) Å, which agrees well with the value of experiment (6.436 Å) [38]. The phonon dispersion and density of states are presented in the figure S1 (https://stacks.iop.org/NJP/23/103043/mmedia) of supplemental materials. We find the frequencies of phonon states at \( \Gamma \) are triply degenerate due to the cubic symmetries of K\(_2\)O. Moreover, the optical phonons with higher frequencies mainly come from the contributions of O with smaller atomic mass, while heavier K atoms mainly contribute to the low-frequency acoustic branches. However, because the electronegativity of O is much larger than that of K, K\(_2\)O is a typical strongly-polarized ionic crystal. An additional non-analytical term correction of polarization field must be considered [17, 39] for the optical phonons around \( \Gamma \). The phonon dispersion after considering the correction is shown in the figure 2(a). The triply degenerate modes with the highest frequencies split into the double-degenerate phonon states and nondegenerate phonon state. Interestingly, two crossing points (D\(_1\) and D\(_2\) in figure 2(a)) are located on the path of \( \Gamma \)–K and at W point around the frequency of 7.5 THz. According to the enlarged figures of figure 2(a), we find the two crossing bands are Dirac-like linear around D\(_1\) and semi-Dirac-like dispersion around D\(_2\). To determine whether these two degenerate points are isolated, we calculate the difference of the frequencies between two intersecting bands and three-dimensional bands in the plane of \( \Gamma \)–K–W–X (see figure 3(a)), as shown in figures 2(c) and (d). The results reveal that the two modes that have the highest frequencies form a nodal ring around high symmetry point X (0.5, 0.5, 1.0) and D\(_1\), D\(_2\) are just a part of the nodal ring. More importantly, the frequency difference of the crossing point is very small and the biggest difference is only 0.1 THz (see figure 2(d)). After considering all symmetry operations of space group \( Fm\bar{3}m \), we find the ring is not isolated and all equivalent nodal rings, which are related by crystal symmetries, connect at the W points in the reciprocal space and form a nodal chain (see figure 1(b)).

The \( \Gamma \)–K–W–X plane is a typical mirror-invariant plane. To demonstrate the nodal rings that form the nodal chain are symmetrically protected or accidental, we calculate the mirror eigenvalues of the vibration modes around the crossing points. The results in the inset of figure 2(a) show that they have opposite mirror eigenvalues, which indicates the nodal rings are robust if mirror symmetries are not breaking. To illustrate the nontrivial topological properties of the nodal chain, we calculate the Berry phase of phonon wavefunction along the paths of figure S2. As we expected, it is equal to \( \pi \) for the nodal ring and 0 for the connected point. These values fulfill the typical characters of a nodal chain.

Topological protected nodal rings generally result in nontrivial surface states. In figures 3(a) and (b), we present the projection of the first Brillouin zone along (001) direction and the projected positions of the nodal rings in different planes. To reveal the nontrivial surface states around normal crossing points (such as D\(_1\)) and the connecting points of a nodal chain (such as D\(_2\)), we choose the paths of cut1 and cut2 (see figure 3(b)) in surface Brillouin zone. In our calculations, the iterative Green’s function method based on a phonon Hamiltonian [40, 41] is used and the calculated phonon local density of states (LDOS) projected on the semi-infinite (001) surface are shown in figures 3(c) and (d). For the result of cut1, we can clearly observe four projected crossing points and drumhead-like surface states between them. Moreover, the projected bulk states still keep the linear character around the crossing points. However, only two projected
Figure 2. (a) Phonon dispersion of K\textsubscript{2}O along \textgamma–L–W–X–U high symmetry paths in the Brillouin zone. The intersections we focus on are circled in red, labeled with D\textsubscript{1} and D\textsubscript{2} respectively. The enlarged band structures around D\textsubscript{1} and D\textsubscript{2} are given and classified by opposite mirror eigenvalues \pm 1. (b) The shape of nodal ring. The color map shows the frequency difference between two bands which form the nodal ring. All relevant high symmetry points and high symmetry paths are marked. (c) Three-dimensional band structure near a nodal ring. (d) The frequency values corresponding to the band crossings which form a nodal ring.

crossing points exist for cut 2 and nonlinear bulk projected states can be observed around these points.

To grasp the formation mechanism of the nodal chain in K\textsubscript{2}O, we build a two-band tight-binding model with the basis of s-orbital-like state on each site for a NaCl-like structure (figure 4(a)). Here we only consider the nearest-neighbor (NN) and third-nearest-neighbor (TNN) hopping interactions, which are illustrated with the cyan and yellow or magenta connecting lines in figure 4(a), respectively. The different colors for TNN are used to represent the opposite signs of the hopping terms (see figure 2(a)). By transforming the model into momentum space, the Hamiltonian is written as:

$$H(k) = d_x(k)\sigma_x + d_y(k)\sigma_y,$$

where $d_x(k) = t_1 (\cos k_x + \cos k_y + \cos k_z)$ and $d_y(k) = t_2 \sin k_x \sin k_y \sin k_z$, $t_1$ and $t_2$ are the NN and TNN hopping amplitudes respectively and $\sigma_x$ and $\sigma_y$ are Pauli matrices for the sublattices. In our calculations, we choose the parameters $t_1 = 0.4$, $t_2 = 0.1$. By diagonalizing the Hamiltonian, we obtain $E_{\pm}(k) = \pm \sqrt{d^2_x(k) + d^2_y(k)}$, which are plotted along the high symmetry lines in figure 4(b). Similar to the phonon dispersion of K\textsubscript{2}O obtained from the first-principles calculation, we find two band degenerate points are formed at W and a $k$-point on the path of \textgamma–K. If the whole three-dimensional Brillouin zone is considered, the situations for the degeneracy of the two bands are $d_x(k) = 0$ and $d_y(k) = 0$. The solution of the previous equation is a periodical six-way valve, which is illustrated with the green surface in figure S3.

The latter equation asks $k_x, y, z = n\pi$ ($n$ is an integer). By combining the solutions of these two equations, we find a series of connected rings are formed, as shown the rings in figure S3. It is worth to note that the positions of the rings in $(2n+1)\pi$ plane and $2n\pi$ are different. Taking the $k_z = 0$ and $k_z = \pi$ planes as
Figure 3. The phonon topological surface states of K₂O. (a) The bulk Brillouin zone and projection plane (001). (b) Schematic diagram of all nodal ring features on the projection plane (001). The lines with different colors correspond to the projected rings in different planes. (c) and (d) LDOS projected on (001) surface along the green and orange dotted line marked in (b). The bright yellow lines represent the surface states, while the dark blue regions represent the projection of bulk bands.

Figure 4. (a) Schematic diagram of the hopping interactions in the tight-binding model. The red and green spheres, respectively, represent inequivalent atoms in a fcc crystal. The six dark cyan sticks indicate the NN hoppings (\(t₁\)). The yellow (\(t₂\)) and magenta sticks (\(-t₂\)) represent the TNN hoppings and different colors indicate their opposite signs. (b) Band dispersion diagram obtained from the tight-binding model. (c) Schematic diagram of the nodal chain structure described by the tight-binding model.

example, for the \(k_z = 0\) plane, the equation that describe the nodal rings is \(\cos k_x + \cos k_y = -1\), but \(\cos k_x + \cos k_y = +1\) for \(k_z = \pi\) plane, which make the center of the rings are \((\pi, \pi, 0)\) and \((0, 0, \pi)\), respectively. By examining all these nodal rings in three-dimensional reciprocal space, we find a nodal-chain is formed and share the same topological nature.

By summarizing the nodal chain in K₂O and other reported systems, we can obtain all possible situations for the appearance of nodal chains and they are illustrated in figure 5. All cases can be classified into two types: the nodal rings are tangent to a \(k\)-point on high symmetry lines (figures 5(b) and (c)) or a
Figure 5. Schematic diagram of band symmetric characteristics. (a) Shows a high symmetry line formed by two perpendicular mirrors marked by red and blue respectively. (b) and (c) Show two cases of energy bands formed by opposite mirror eigenvalues on high symmetry lines, (d) and (e) show two cases at the high symmetry point. The green and red dots represent high symmetry points and the points on a high symmetry line, respectively. The nodal chain we have discovered belongs to the latter.

high symmetry point (figures 5(d) and (e)), and we name them as type-I and type-II, respectively. In our paper, a high symmetry point means the symmetry of this point is higher than that of all the surrounding points. In either case, the mirror eigenvalues of the two crossing nondegenerate bands or double degenerate bands must be opposite for the two intersecting mirrors. If the intersection point is on the high symmetry line, the two crossing bands generally are linear around the crossing points. However, if the crossing point is at a high symmetry point, the dispersion of the bands generally are quadratic due to more symmetry operations exist in the little group of the \( k \)-point.

By detailedly analyzing the characters of nodal chains, we can obtain some general rules about the existence of a nodal chain in a system with symmorphic space groups: (i) two mirror-invariant planes and two nodal rings formed in these planes are protected by the mirror symmetries with opposite mirror eigenvalues (see figure 5); (ii) a band crossing or double degenerate point must exist on the high symmetry lines formed by two orthogonal mirror-invariant and the two crossing bands must have opposite mirror eigenvalues (see figures 5(b)–(e)). The crossing point or double degenerate point must be a part of the two rings in mutually orthogonal planes; (iii) the intersection lines should not be a \( C_n \) or \( S_n \) (\( n = 3, 4, 6 \)) rotation axis. If this rule is not fulfilled, more than two rings would connect by a \( k \)-point on the lines. (iv) If the intersection lines are \( C_2 \) rotation axis, the lines must pass through the center of the rings (see figure S4(a)) and cannot be tangent to the rings (see figure S4(b)). Clearly, this rule would make sure all rings in a mirror-invariant plane are not connected. It must be noted that these rules only can be applied to a spinless system.

According to these rules, we obtain all symmorphic space groups in which a type-I nodal chain may exist. It is noted that we only consider the space groups in which no more than two nonequivalent mirrors exist. The information about these space groups are listed in table S1. Here we use the example of space group \( P\bar{6}m2 \) to illustrate the nodal chain in the low-energy electronic states of HfC when SOC is not considered [16]. For HfC, a pair of mutually orthogonal mirror-invariant planes in reciprocal space are \( k_z = 0 \) and \( k_x = 0 \) (other vertical mirror-invariant plane are equivalent to it). The intersection line of these two planes is high symmetry line \( \Gamma \)-M. According to the energy bands structure of reference [16], we find two nondegenerate bands form a linear crossing with opposite mirror eigenvalues on this line. By concretely calculating all characters of the operations in the little group, we find the nodal chain in HfC fulfill the situation of figure 5(c) with the little group representations of \( \Sigma_2 \) and \( \Sigma_3 \). For type-II nodal chain, the rules (iii) and (iv) must be applied to any axis that passes through the high symmetry points. By analyzing all the end points of high symmetry lines in table S1 and high symmetry points of other symmorphic space groups, we found a nodal chain connected at high symmetry points can be formed only in the systems with the space group \( Fm\bar{3}m(225) \). The rotation operations that make the nodal chain cannot be formed are listed in table S2. Take the \( \Gamma \) point of space group \( P\bar{6}m2 \) as an example. \( C_6 \) exist in the wavevector group of \( \Gamma \). If nodal rings connect at this point, this rotation operation would ask three equivalent rings are inscribed at \( \Gamma \), as shown in figure S5.

Except K2O, similar nodal chains can be found in the phonon dispersions of other alkali metal oxides or sulfides, including Li2O, Na2O, Rb2O, K2S and Rb2S (see figure S6). Most of these materials have been synthesized in experiments. We expect the nodal chain in these materials can be measured by x-ray scattering [33, 42] or neutron scattering [43] and the nontrivial surface states can be probed by high
resolution electron energy loss spectroscopy [44], helium scattering [45], or THz spectroscopy [46, 47]. Moreover, we expect K$_2$O materials class will provide a platform to study the effect of a phonon nodal chain to the thermodynamic properties of materials. Certainly, our discussion of nodal chain can be generalized to any system described by a single space group, such as the electronic systems if the SOC of electrons is negligible.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

P Zhou https://orcid.org/0000-0002-5570-2427

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