Orbital-hybridization-created optical excitations in Li$_8$Ge$_4$O$_{12}$

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Li$_8$Ge$_4$O$_{12}$, a ternary electrolyte compound of Li$^+$-based battery, presents the unusual essential properties. The main features are thoroughly explored from the first-principles calculations. The concise pictures, the critical orbital hybridizations in Li-O and Ge-O bonds, are clearly examined through the optimal Moiré superlattice, the atom-dominated electronic energy spectrum, the spatial charge densities, the atom- and orbital-decomposed van Hove singularities, and the strong optical responses. The unusual optical transitions cover the red-shift optical gap, 14 frequency-dependent absorption structures and the most prominent plasmon mode in terms of the dielectric functions, energy loss functions, reflectance spectra, and absorption coefficients. Optical excitations, depending on the directions of electric polarization, are strongly affected by the excitonic effects. The close combinations of electronic and optical properties can identify a significant orbital hybridization for each available excitation channel. The developed theoretical framework will be very useful in fully understanding the diverse phenomena of cathode/electrolyte/anode materials in ion-based batteries.

I. INTRODUCTION

Lithium-ion batteries (LIBs) dominate in commercial purposes due to their high-performance energy resources, e.g., high power, energy densities, and high reliability, as well as other certain fundamental merits including affordable price, long cycle life, and friendly environment [1,3]. The recent experimental progress shows many applications of LIBs such as electric vehicles (EV) and hybrid EV and mobile devices, which require the optimum in producing efficient energy. A Li-ion battery principally consists of a cathode (positive electrode), an anode (negative electrode), and an ionically conductive Li$^+$-containing electrolyte, in which the third component is closely related to the unusual transport of the positive lithium ions (Li$^+$) between two electrodes [1,3]. Depending on the combined alternative materials of three components, Li-ion batteries could provide various performance, e.g., the specific energy density in the values of 100 to 250 W.h/Kg [4,5], the volumetric energy density from 250 to 680 Wh/L [6], the specific power density in the range of 300 to 1500 W/kg [7,8], and the faster charging time (80 % of charge of states in 15 mins) [9]. The critical mechanisms of LIBs are characterized by the specific charging and discharging process which is based on the exchange of Li$^+$-ions. During the charging process, Li$^+$-ions commonly move from the cathode material and transport externally to intercalate into the anode through the electrolyte. When discharging, the electrons flow from the anode to the cathode through an outer circuit creating an electric current, mainly converted chemical energy into electrical energy. Most importantly, the electrolyte plays an important role during the charging-discharging process, however, recently electrolyte used in Li-ion batteries is not compatible with latterly developed high-voltage positive electrodes, which are one of the most effective ways of increasing the energy density. Nowadays, solid electrolytes are now rapidly emerging as promising alternatives given their wider electrochemical window of stability [10]. As potential electrolyte candidates, Li-Ge-O compounds exhibit the large ionic conductivity (1.5×10$^{-5}$Ω.cm$^{-1}$ for Li$_2$GeO$_3$), in which electronic conductivity is negligible with a high ionic transference number [10]. Furthermore, Li$_2$GeO$_3$ shows wide cycling stability with a reserved charge capacity of 725 mAh$^{-1}$ after 300 cycles at 50 mAg$^{-1}$ [11]. As for the battery safety, Li$_2$GeO$_3$ is suitable for the selection of solid electrolytes according to the reasonable decreasing in interface resistance.

Recently, a lot of high-resolution experimental measurements on essential physical properties of anodes/cathodes/electrolytes in the Li$^+$-based batteries, e.g., optimized geometry structures, band structures, optical properties and transport. The X-Ray diffraction and the low-energy electron diffraction (LEED; [12]) are available in investigating the 3D lattice symmetries, especially Li-X-O related systems. The angle-resolved photoemission spectroscopy (ARPES, [13]) is a powerful experimental technique directly measuring the single particle spectral function, depending on wave vectors and frequency. For example, ARPES could measure the Dirac cone structure of AA/AB bilayer graphene, the band energy dispersion along the synthetic dimension, band gap, and so on. There are many methods developed for measuring optical properties, for example, the complex permittivity, which is based on the constraints in specific frequencies, materials, applications could be measured by transmission/reflection line method [14], open-ended coaxial probe method [14], free space method [14], resonant method [14]. Other optical properties, such as energy loss functions, reflectance, absorbance, refractivity, excitation could be found through spectroscopy measure-
ments, for example, analysis of the specular reflection from the polished surface of a solid can give the complex index of refraction using the Kramers-Kronig method. Recently, Li-Ge-O compounds have a few delicate experimental measurements, such as X-Ray diffraction [11] and one photoluminescence with excitation measurement [15]. Up-to-day, concise physical and chemical pictures are not proposed for the essential properties of the Li-Ge-O compound. Furthermore, the theoretical electrolytes related to Li-Ge-O compounds with band structures, optical properties and other predictions about chemical/physical combinations are still absent. In this work, we have connected the theoretical study on geometric/physical environment.

We used the density functional theory (DFT) method via the Vienna Ab-initio Simulation Package (VASP) [19] to perform the optimization of structure and calculation the electronic and optical properties. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation was used for the exchange-correlation functional [20]. The interaction between the ions and valence electrons was described by the projector augmented wave (PAW) method [21]. The cutoff energy for the expansion of the plane wave basis set is 600 eV. The Brillouin zone was integrated with a special k-points mesh of 11×11×11 in the Monkhorst-Pack sampling technique to obtain the corrected density of states, electronic band structure and quasi-particle excitations of Li$_8$Ge$_4$O$_{12}$. Regarding the optical response beyond the independent particle approach, the electron-hole interaction was taken into account by solving the standard Bethe-Salpeter equation (BSE) within the Tamm-Dancoff approximation [24]. The k-point sampling, energy cutoff, and number of bands setting the same as in the GW calculation. In this calculation, the 20 highest occupied valence bands (VBs) and 15 lowest unoccupied conduction bands (CBs) are included as a basis for the excitonic states with the photon energy region from 0 eV to 23 eV. In addition, the broadening parameter γ, which arises from various de-excitation mechanisms, was set at 0.15 eV to make the spectrum more accurate for the given k-point meshes. All parameters in this study have been checked for the convergence of the calculations.

III. RESULTS AND DISCUSSIONS

The ternary compound, Li$_8$Ge$_4$O$_{12}$ with 24 atoms within a unit cell, is chosen for a model study in illustrating the geometric, electronic and optical properties. The optimal lattice, as clearly shown in Fig. 1(a), belongs to an orthorhombic structure. Each Li/Ge atom is surrounded by four O atoms in the tetrahedral form. There exist 32 Li-/16 Ge-O bonds, in which the former and the latter display the large fluctuations about their lengths (∼1.93-2.12 Å and ∼1.72-1.84 Å respectively). The calculated lattice constants along $x$-, $y$- and $z$-directions, (9.61, 5.46, 4.87 Å), are very close to the X-ray diffraction measurements, (9.60, 5.50, 4.85 Å) in Ref.[11] and (9.63, 5.48, 4.84 Å) in Ref.[23]. Obviously, the greatly non-uniform chemical/physical environment indicates the importance of orbital hybridizations in chemical bondings. Furthermore, it might be very useful for supporting the ion transport in electrolyte materials. This behavior will be responsible for the unusual effects of Moiré superlattice and the highly anisotropic optical transitions.

Li$_8$Ge$_4$O$_{12}$ exhibits the rich and unique band structure. The main features in Fig. 2(a) cover a lot of valence and conduction subbands in a wide energy range (-22 eV < $E^{c,v}$ < 14 eV), the high asymmetry of hole and electron energy spectra about the Fermi level ($E_f = 0$). An indirect band gap of $E_g^{i} = 3.8$ eV related to the highest occupied state and the lowest unoccupied one, respectively, at $Z$ and $Γ$ points, the parabolic/oscillatory/linear/partially flat energy dispersions with various band-edge states, and the atom-dominated electronic states at the different energy regions. Very interestingly, such results are associated with many significant orbital hybridizations in Li-O and Ge-O bonds, being clearly identified from the close combinations of the atom- and/or orbital-dependent
The electronic structure could be classified into four categories according to the various atoms’ and orbitals’ contributions, as clearly indicated by in Figs. 2(b), 2(c) and 2(d) by green, blue and red circles for Li, Ge and O, respectively. (I), (II), (III) and (IV) regions, respectively, correspond to $E^c > 5.4$ eV, $1.89$ eV $< E^c < 5.15$ eV, $-6.0$ eV $< E^c < -1.89$ eV, $-9.1$ eV $< E^c < -6.0$ eV, and $-21$ eV $< E^c < -17.0$ eV. It should be noticed that valence subbands disappear between (III) and (IV) regions. The Li atoms only make very weak, but significant contributions within a whole range of band structure (small radii in Fig. 2(b)), i.e., the unusual essential properties disappear in the absence of Li-O bonds. The energy-spectrum subgroups are qualitatively characterized by (I) (Ge, O) co-dominance, (II) O dominance, (III) (Ge, O) co-dominance, and (IV) O dominance, being supported by the atom- and orbital-projected density of states (discussed later in Fig. 4). The specific orbital hybridizations in chemical bonds will be identified to be associated with the critical energy bands in revealing the prominent absorption structures.

The spatial charge distributions before/after chemical bondings can provide some very useful information about the first-step orbital hybridizations in Li-O and Ge-O bonds. An isolated Li atom has an isotropic charge density (Fig. 3(a)), in which the inner and outer regions (the red and green parts) arise from $1s$ and $2s$ orbitals, respectively. The similar, but wider distribution, which corresponds to the O case (Fig. 3(b)), is associated with $(1s, 2s)$ and $(2p_x, 2p_y, 2p_z)$ orbitals. Furthermore, the highest charge density appears around Ge (Fig. 3(c)), with the separate ranges of $(4s, those below it)$ and $(4p_x, 4p_y, 4p_z)$ orbitals. As for Li-O bonds, the outer/inner regions show the obvious/minor deformations along three electric-polarization directions (Figs. 3(g)-(i)), especially for the neighboring ones. These clearly indicate the multi-orbital hybridizations of $2s-(2p_x, 2p_y, 2p_z)$, the single-orbital hybridization of $2s-2s$. In addition to the green regions (Figs. 3(g)-(i)), the red ones near O and Ge atoms present the observable changes, suggesting the significant bondings of $(4s, 4p_x, 4p_y, 4p_z)-(2s, 2p_x, 2p_y, 2p_z)$. While the above-mentioned analyses are combined with the atom- and orbital-projected van Hove singularities, the orbital-hybridization-dominated band-edge states will be identified. They are responsible for a lot of strong absorption structures (Figs. 5 and 6).

The atom- and orbital-projected density of states (Fig. 4), being supported by the atom-dominated band structure (Fig. 2) and charge density distribution (Fig. 3).
FIG. 3. Compared with an isolated (a)/(b)/(c) Li/Ge/O atom, the spatial charge distributions related to the significant orbital hybridizations in (d)/(e)/(f) Li-O and (g)/(h)/(i) Ge-O bonds along the x-/y-/z-directions for the shortest chemical bonds.

3), can clearly identify the energy-dependent orbital hybridizations. They come from the band-edge states of various energy dispersions, such as, the extreme, saddle and dispersionless ones. Both critical points in energy-wave-vector spaces and dimensionality fully determine their special structures [17]. As a result of too many subbands and broadening effects, Fig. 4(a) only displays the prominent asymmetric peaks and shoulders (the black curve). The van Hove singularities of different atoms/orbitals can merge together (Figs. 4(a)-4(d)), clearly indicating the specific orbital hybridizations. According to their strong co-relations, the five subgroups of band structure are further examined to be dominant through (I) 2s-(2s, 2p\textsubscript{x}, 2p\textsubscript{y}, 2p\textsubscript{z}) & (4s, 4p\textsubscript{x}, 4p\textsubscript{y}, 4p\textsubscript{z})-(2s, 2p\textsubscript{x}, 2p\textsubscript{y}, 2p\textsubscript{z}), (II) 2s-(2p\textsubscript{x}, 2p\textsubscript{y}, 2p\textsubscript{z}) & 4s-(2p\textsubscript{x}, 2p\textsubscript{y}, 2p\textsubscript{z}), (III) 2s-(2p\textsubscript{x}, 2p\textsubscript{y}, 2p\textsubscript{z}) & (4s, 4p\textsubscript{x}, 4p\textsubscript{y}, 4p\textsubscript{z})-(2p\textsubscript{x}, 2p\textsubscript{y}, 2p\textsubscript{z}), (IV) 2s-(2p\textsubscript{x}, 2p\textsubscript{y}, 2p\textsubscript{z}) & 4s-(2p\textsubscript{x}, 2p\textsubscript{y}, 2p\textsubscript{z}) and (V) 2s-2s & 4s-2s. Such identifications of significant orbital bondings would become more delicate under the strong optical responses, mainly owing to the greatly reduced energy width of excitation frequency.

The imaginary and real parts of dielectric function are very useful in understanding the available optical transitions, and they can fully examine the orbital-related prominent responses by linking the atom-dominated band structure (Fig. 2), charge density (Fig. 3), and atom - & orbital-decomposed van Hove singularities (Fig. 4). The former (ε\textsubscript{2}(ω)), as clearly shown in Fig. 5(a), presents the excitation characteristics of available channels in the absence of screening effect of all valence charges. An optical gap (E\textsubscript{g}), which corresponds to the threshold absorption frequency, is about 2.50/2.55/2.35 eV under the many-body effects for the x-/y-/z-directions of electric polarizations (the black/red/blue curves). However, it is ~ 4.00 eV purely subbands and the square of the electric dipole moment, respectively, corresponding to the number and intensity of available optical transitions. The excited valence holes and conduction electrons simultaneously come into existence during the optical excitations; furthermore, they could strongly combine together through the attractive Coulomb potentials under the suitable condition, e.g., the large band gap for the suppression of temperature broadening. The coupled quasiparticles, the stable excitons, might strongly affect the main features of optical absorption spectra, since they make important contributions to many-body effects. That is, they take part in the various-order excitation processes using the Coulomb scatterings, leading to the dramatic transformations of photons. The excitonic effects, which are closely related to the critical orbital hybridizations, are the studying focus.

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FIG. 5. (a) The imaginary- and (b) real-parts of dielectric functions with the excitonic effects under three electric-polarization directions [the black, red and blue curves]. Comparison of the imaginary parts of dielectric function without (c) and with (d) excitonic effects under xx-polarization direction.

through the single-particle optical excitations for $E_{\parallel \hat{x}}$ (the black curve in Fig. 5(c)). Compared with band gap of $E_g = 3.8$ eV, the great red shift clearly indicates the very strong Coulomb couplings between the excited holes and electrons. The composite quasiparticles should be quite stable, so that they are expected to survive at room temperature. The theoretical predictions are relatively easily examined by the various optical spectroscopies [15, 27–29]. Very interesting, there exist 14 pronounced peak/shoulder absorptions (the distinct colored triangles). The frequency-dependent vertical transitions and orbital hybridizations are identified by the delicate analyses (the details in Table 1). Such unusual results are achieved from the concise physical and chemical pictures in atom-dominated band structure (Fig. 2), atom-, orbital-decomposed density of states (Fig. 4), and strong optical responses due to band-edge states. This delicate analysis is expressed as below.

In the absence of many-body effects, the vertical transitions from the occupied to the unoccupied states lead to the finite amplitude of the absorption function. The appearance of certain special optical-spectral structures is associated with transitions from band-edge states/band dominated/Van Hove singularities of electronic band structure/atom-dominated band structure/orbital-projected density of states. As for Figs. 5(c), S1(a) and S2(a) in supporting information show plots of the imaginary part of dielectric function without excitonic effect for $x$-, $y$- and $z$-directions of polarizations, respectively. We observe diverse spectral structures, including symmetric, asymmetric peaks and shoulders with various shapes. The corresponding excitation channels are marked with arrow heads in Fig. 2(a) and the triangle in Fig. 4. Generally, these channels are major/minor contributed from the electron transition between O 2p occupied states and Ge 4p/Li 2s unoccupied states. For example, in $x$-direction, the threshold structure is marked by a red triangle in Fig. 5(c), which is due to excitation from the valence flat band to the conduction minimum extremes at the $\Gamma$ point. It is mainly/slightly dominated by the O-2p, valence states and the Ge-4s/Li-2s conduction ones, indicated by the red arrow head in Fig. 2(a) and the red triangle in Fig. 4, respectively. The different atomic arrangements can give different electric dipole matrices. Therefore, the excitation intensities may cause serious differences under $x$-/ $y$-/ $z$-directions of the electric polarization. However, their energies are almost the same because of the identity of the joint density of states. Furthermore, the electron-hole Coulomb interaction causes series excitation peaks to appear just below the band gap, and modify the absorption coefficient just above the band gap. The latter is a consequence of the overlap increasing of the hole and electron, thereby leading to change the transition probability, e.g the existence of three prominent peaks in the $\epsilon_2(\omega)$ (Fig. 5(d)), in which the third peak with strong intensity just appears at the optical gap in Fig 5(c). The electron-hole interaction triggers a redshift of the onset optical transition energies and also modifies their relative absorption intensities. However, it cannot strongly modify the intrinsic chemical bondings. Therefore, the excitation rule as mentioned above is suitable for the case that includes the excitonic effect (as clarified in Figs. 5(c)-5(d) and Table 1). Using this strategy, the specified mechanisms for the various absorption structures could be achieved, is never revealed in the previous studies. This viewpoint has been successfully generalized to anode and cathode materials of Li$^+$-based batteries.

As for $\epsilon_1(\omega)$ (Fig. 5(b)), their prominent absorption structures could be understood from those of $\epsilon_2(\omega)$ (Fig. 5(a)) by the Kramers-Kronig relation under the
TABLE I. Prominent absorption structures: frequencies, colored indicators and identified orbital hybridizations

| Excitation frequency (eV) | Colors of arrows | Specific orbital hybridizations in Ge-O bonds |
|---------------------------|------------------|---------------------------------------------|
| With excitonic effect      | Without excitonic effect |                                               |
| 2.7                       | –                | –                                           |
| 3                         | –                | –                                           |
| 3.9                       | Red              | Ge(4s) - O(2p_z)                            |
| 5.6                       | Orange           | Ge(4s) - O(2p_y,2p_z)                       |
| 6.6                       | Purple           | Ge(4s) - O(2p_y)                            |
| 8                         | Green            | Ge(4s) - O(2p_y)                            |
| 9.1                       | Blue             | Ge(4p_y,4p_z) - O(2p_y)                    |
| 10.5                      | Brown            | Ge(4s,4p_x,4p_y,4p_z) - O(2p_x,2p_y,2p_z)   |
| 11.5                      | Yellow           | Ge(4p_x,4p_y,4p_z) - O(2p_x,2p_y,2p_z)      |
| 12.1                      | Pink             | Ge(4s,4p_x,4p_y,4p_z) - O(2p_x,2p_y,2p_z)   |
| 13.9                      | Grey             | Ge(4p_y,4p_z) - O(2p_x,2p_y,2p_z)           |
| 15                        | Light-blue       | Ge(4p_y) - O(2p_x,2p_y,2p_z)               |
| 16.8                      | Violet           | Ge(4p_y,4p_z) - O(2p_x,2p_y,2p_z)           |
| 18.8                      | Light-green      | Ge(4p_x,4p_y,4p_z) - O(2p_x,2p_y,2p_z)      |

event of optical excitations. Apparently, the van Hove singularities in \( \epsilon_1(\omega) \) and \( \epsilon_2(\omega) \) might be similar or different, being strongly co-related by the principal-value integration on the complex plane. Below the threshold frequency, \( \epsilon_1(\omega) \) weakly depends on \( \omega \), in which its value roughly lies within the range of 2.9-3.0 for \( x-, y- \) polarizations and \( z \) one. This will determine the low-frequency reflectance spectrum (Fig. 6(b)) and the vanishing absorption coefficient (Fig. 6(c)). Very interesting, \( \epsilon_1(\omega) \) is very sensitive to the changes of frequency during the creation of the excited holes and electrons. It could vanish at the weak Landau damping, in which its zero point and the small \( \epsilon_2(\omega) \) might appear simultaneously, e.g., the vanishing \( \epsilon_2(\omega) \) at 16.0/15.2 eV under \( \mathbf{E}||\mathbf{x}/\mathbf{E}||\mathbf{y} \) (the black/red curves). In addition, the zero points for the \( z \)-polarization (the blue curve) become meaningless because of the combination with very strong electron-hole excitations.

The energy loss function (ELF), being defined as \( \text{Im} \left[ \frac{1}{\epsilon(\omega)} \right] \), is the screened response function due to the significant valence charges of Li, Ge and O atoms. The charge screenings can determine the coherent carrier oscillations at the long wave-length limit during the optical transitions. In general, the collective excitations (a plasmon mode) are revealed as a sufficiently strong peak with ELF higher than 1, as clearly indicated in Fig. 6(a). The strongest peak comes to exist at \( \omega_p=16.0/15.5/15.0 \) eV for the \( x-/y-/z \)-direction electric polarizations, being attributed to the significant orbitals of Li-2s, O-(2p_x, 2p_y, 2p_z) & Ge-(4s, 4p_x, 4p_y, 4p_z). The O-2s contribution for the most prominent plasma wave is ignored, since its dominating valence states only appear below -17.5 eV (the black curve in Fig. 4(d)). In addition, few minor plasmon peaks are accompanied by the serious Landau dampings. It should be noticed that two manners could be utilized to identify the collective excitations, but the current peak in ELF is much better than the zero points in \( \epsilon_1(\omega) \). The absence of the latter and/or the combination with a very large \( \epsilon_2(\omega) \) is the main reason.

The reflectance spectrum is characterized as \( \text{R}(\omega)=\frac{\sqrt{\epsilon(\omega)-1}}{\sqrt{\epsilon(\omega)+1}} \) [31], when an electromagnetic wave is normally incident on Li_8Ge_4O_18. The total electric field will be reflected by the surface, absorbed by the valence electrons and transmitted through a finite-width sample. Both reflectance R(\omega) and absorption coefficient \( \alpha(\omega) \) are inverse of propagation decay length in [32], as shown in Figs. 6(b) and 6(c), respectively, directly reflect the main features of single-particle (Figs. 5(a) and 5(b)) and collective excitations (Fig. 6(a)). For \( \omega < E_{g} \), a small reflectance weakly depends on frequency, and it is roughly given by \( \frac{\sqrt{\epsilon(\omega)-1}}{\sqrt{\epsilon(\omega)+1}}^2 \). \( \alpha(\omega) = 0 \) because of the vanishing electron-hole excitations, leading to the non-decay EM-wave propagation and thus a very efficient transmission. However, within the active region of valence-electron excitations (\( E_{g} < \omega < 20 \) eV), the sensitive and significant frequency dependences come to exist. Reflectance is enhanced and displays a large fluctuation under the various inter-band excitation channels, in which the drastic change of plasmon edge appears at \( \omega_p \), e.g., \( \sim 40\% \) variation under the \( \mathbf{E}||\mathbf{x} \) case (the red curve). Moreover, \( \alpha(\omega) \) is very large, especially that related to the plasmon mode, and its inverse is about 0.7-4.0 Å, the EM waves are easily absorbed by Li_8Ge_4O_18 thorough the rich electronic excitations.

In addition to X-ray diffractions [11, 24], only very few experimental examinations on electronic and optical properties. In general, the wave-vector dependences of occupied valence states could be directly tested by the angle-resolved photoemission spectroscopy (ARPES) [13, 33]. A lot of unusual energy subbands (Fig. 2) due to a Moiré superlattice would create high barriers in
FIG. 6. The various optical properties: (a) energy loss functions, (b) reflectance spectra, and (c) absorption coefficients.

the ARPES measurements. Scanning tunneling spectroscopy (STS) is available for the clear identification of van Hove singularities near the Fermi level [34]. However, STS might be suitable only under a thin-film sample because of very weak quantum currents. Very interestingly, the optical spectroscopies of reflectance [26], absorption [27] and transmission [28] are reliable in verifying the frequency-dependent optical properties. For example, the measured reflectance spectrum, being supported by the Kramers-Kronig relations between \( \epsilon_1(\omega) \) and \( \epsilon_1(\omega) \), is able to determine both of them. It provides significant information about the initial excitonic peaks, the greatly reduced threshold excitation frequency, many prominent absorption structures, and the strongest plasmon mode at \( \omega_p > 16 \) eV. Up to now, one photo-luminescence measurement has verified the first excitonic peak at \( \sim 2.70 \) eV [15], being close to the current prediction of \( \sim 2.55 \) eV. Apparently, the diverse optical properties in cathode/electrolyte/anode materials of Li\(^{+}\)-based batteries are worthy of systematic investigations both experimentally and theoretically.

IV. CONCLUSION

The significant orbital hybridizations in chemical bonds, being based on the first-principles calculations, are thoroughly identified for the Li\(_8\)Ge\(_4\)O\(_{12}\) compound in terms of the geometric, electronic and optical properties. They will play important roles in fully understanding the diversified essential properties of cathode/electrolyte/anode materials in ion-related materials. This solid-state electrolyte presents the unusual features, the Moiré superlattice with a highly non-uniform chemical environment, the Li-, O- or Ge-dominated energy bands, the orbital-induced spatial charge densities, the atom- and orbital-decomposed van Hove singularities. As a result, the band-edge ones, which might create the prominent optical responses, are well characterized by the specific orbital interactions through the developed theoretical framework. The featured optical transitions cover a red-shift optical gap (\( E_o^g = 2.55 \) eV) much lower than an indirect one (\( E_i^g = 3.8 \) eV), a very long transmission length/low reflectance for \( \omega < E_o^g \), fourteen pronounced single-particle absorption structures (short decay lengths), and the most strong plasmon peak/a quickly decreasing edge in energy loss function/reflectance spectrum at \( \omega_p, 15-16 \) eV, and the sensitive changes due to the electric-field directions. The many-body excitonic effects have strongly modified the single-particle interband excitations. Under the current investigations, the developed theoretical framework is further generalized to other electrolyte/cathode/anode materials of Li\(^{+}\)-based batteries.

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[1] G. Pistoia. *Elsevier*, 2014, 664.
[2] D. Deng. *Energy. Sci. Eng* 2015, 3(5), 385-418.
[3] M. Li, J. Lu, Z. Chen, K. Amine. *Adv. Matter* 2018, 30, 1800561.
[4] Y. Kato, S. Shiotani, K. Morita, K. Suzuki, M. Hirayama, R. Kanno. *J. Phys. Chem. Lett.* 2018, 607613.
[5] Nam, Y. J.; Oh, D. Y.; Jung, S. H.; Jung, Y. S. *J. Power Sources* 2018, 375, 93101.
[6] J. Quinn, T. Waldmann, K. Richter, M. Kasper, M. W-Mehrens. *J. Electrochem. Soc.* 2018 165 (14): A3284A3291.
[7] G. E .Blomgren. *J. Electrochem. Soc.* 2017, 164, A5019A5025.
[8] C. Sun, J. Liu, Y. Gong, D. P. Wilkinson, J. Zhang. *Nano Energy* 2017, 33, 363386.
[9] X. G. Yang, G. Zhang, S. Ge. & C. Y. Wang. *Proc. Natl.Acad.Sci. U.S.A* 2018 115(28), 72667271.
[10] B. E. Liebert, R. A. Huggins. *Mater. Res. Bull* 1976, 11, 533-538.

[11] M. Mokhlesur, R. Irin, Sultana, T. Yang, Z. Chen, N. Sharma, A. Glushenkov, Y. Chen. *Angew. Chem.* 2016, 55, 16059-16063.

[12] Y. Horio. *Springer*. 2018.

[13] M. Mokhlesur, R. Irin, Sultana, T. Yang, Z. Chen, N. Sharma, A. Glushenkov, Y. Chen. *Angew. Chem.* 2016, 55, 16059-16063.

[14] Y. Horio. *Springer*. 2018.

[15] P. Dijana, B. Cynthia, O. Michal, J. H. Booske. *IEEE Transaction on microwave theory and methods*. 2005, 53, 5.

[16] A. N. Trukhin, U. Rogulis, M. Spingis. *J. Lumin.* 1997, 72-74, 889-892.

[17] T. D. H. Nguyen, H. D. Pham, S. Y. Lin and M. F. Lin. *RSC. Adv.* 2020, 10, 14071-14079.

[18] N. T. Han, Y. K. Dien, N. T. Tran, D. K. Nguyen, W. P. Su and M. F. Lin. *RSC Adv.* 2020, 10, 24721-24729.

[19] R. Chen, W. Qu, X. Guo, L. Li and F. Wu. *Mater. Horiz.* 2016, 3: 487-516.

[20] G. Kresse and J. Hafner. *Phys. rev. B* 1993, 47:558-561.

[21] J. P. Perdew, K. Burke, and M. Ernzerhof. *Phys. rev. Lett.* 1996, 77:3865-3868.

[22] G. Kresse and D. Joubert. *Phys. rev. B.* 1999, 59:1758-1775.

[23] P. Wisesa, K. A. McGill and T. Mueller. *Phys. Rev. B*. 2016 93:155109.

[24] M. Shishkin, M. Marsman, and G. Kresse. *Phys. Rev. Lett.* 2007, 99, 246403.

[25] J. Paier, M. Marsman, and G. Kresse. *Phys. Rev. B*. 2008, 78, 121201.

[26] Yin C, H. Xiang, C. Li, H. Porwal, L. Fang. *J. Am. Ceram. Soc.* 2018, 101: 4608-4614

[27] M. Rohlfing and S. G. Louie. *Phys. Rev. B*. 2000, 62, 4927.

[28] M. B. Wallace, A. Wax, D. N. Roberts and R. N. Graf. *Gastrointestinal Endoscopy Clinics of North America*. 2009, 19, 233-242.

[29] J. Jimenez, J. W. Tomm. *Springer*. 2016, 202, 307.

[30] J. M. Dawlaty, S. Shivaraman, Jared Strait, P. George, M. Chandrashekhar., et al. *Appl. Phys. Lett.* 2008, 93, 131905.

[31] J. Y. Wu, S. C. Chen, G. Gumbs and M. F. Lin. *Phys. Rev. B*. 2016, 94, 205427.

[32] S. Saha, T. P. Sinha and A. Mookerjee. *Phys. Rev. B*, 2000, 62, 8828.

[33] S. Liming, X. Zhao, et al. *J. Appl. Phys.* 2010, 108, 093519.

[34] D. Lu, I. M. Vishik, M. Yi, Y. Chen, R. G. Moore, Z. X. Shen. *Annu. Rev. Condens. Matter Phys.* 2012, 3, 129-167.

[35] Y. Niimi, K. Kanisawa et al., *J. Phys. Conf Ser.* 2007, 161, 174.