# Valley quantum interference modulated by hyperbolic shear polaritons

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Recently, symmetry-broken polaritons within low-symmetry crystals have triggered extensive research interest since they present enhanced directionality of polariton propagation for nanoscale manipulation and steering of photons. The latest discovery of hyperbolic shear polaritons (HShPs) in low-symmetry Bravais crystals provides great promise for innovating valleytronics. Herein, we theoretically demonstrate the coherent manipulation of the valley degree of freedom in a two-dimensional valleytronic material interfaced with monoclinic Ga2O3 and CdWO<sub>4</sub> crystals. Robust and wideband tunable valley interference values are achieved in the mid- to far-infrared wavelengths. By virtue of stronger shear effect in monoclinic Ga<sub>2</sub>O<sub>3</sub>, the valley quantum interference fringes modulated by Ga<sub>2</sub>O<sub>3</sub> crystal are more than those tuned via CdWO<sub>4</sub> crystal. After the monoclinic Ga<sub>2</sub>O<sub>3</sub> crystal is doped by free charge carriers, the number of HShP modes gradually decreases accompanied by the blueshifts and broadening of some hyperbolic dispersion bands as the doping concentration increases. In consequence, main fringes of valley quantum interference are broadened and shift toward the short wavelengths. Additionally, the doping increases the optical losses which limit the effective propagation of shear polaritons in monoclinic crystals. Therefore, the valley quantum interference is gradually reduced to a smaller and smaller negative value range as the doping concentration increases in the monoclinic crystal. Finally, the azimuthal dispersion of the HShP propagation direction gives rise to symmetry-broken valley quantum interference patterns when tuning the azimuth and twist angles of monoclinic hybrid structures. The azimuth angles of quantum interference fringes are susceptive to the variation of lattice displacement direction induced via the doping concentration. Thus, the valley quantum interference has great potential in estimating the doping concentration and the propagation directions of HShPs in monoclinic crystals.

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#### I. INTRODUCTION

Over the last few years, valleytronics, as an emerging research area, has drawn particular attention for a variety of potential applications ranging from quantum information processing [1-3] to valley-based optoelectronic devices [4–7]. Valleytronics aims at manipulating the electronic valley degree of freedom in two-dimensional (2D) gapped Dirac systems, such as the transition metal dichalchogenides (TMDCs) and gapped bilayer graphene [6-8]. The electronic band structure of such systems consists of two degenerate yet inequivalent K and K' valleys at the corners of the hexagonal Brillouin zone. Because of the broken inversion symmetry and strong spin-orbit interaction, the excitons (Coulombbound electron-hole pairs) in K and K' valleys are coupled to photons with the same energy but mutually orthogonal polarization helicities  $\sigma_{\pm}$ , respectively. To harness the valley degree of freedom, it is imperative to be able to control the coherence between excitons in these two valleys actively. The coherence among the valleys (optical alignment of excitons), i.e., valley quantum coherence, was first revealed by the observation of a linearly polarized emission (coherent superposition of  $\sigma_+$  photons) from monolayer WSe<sub>2</sub> optically excited by a linearly polarized light [9]. Thus far, it has been proved that to realize the intervalley quantum coherence is one key step toward practical applications with valleytronic materials [10]. Unfortunately, on account of the constraint on intervalley scattering and dephasing arising from phonons and defects, high valley quantum coherence usually occurs only at extreme conditions such as cryogenic temperature or near-resonance excitation [11–14]. Recently, several strategies including integrating 2D gapped Dirac materials with various metastructures and anisotropic 2D materials have been proposed to realize the valley coherence up to room temperature [13–17]. Nonetheless, these efforts are either relatively challenging due to the elaborate microfabrication processes or at the cost of system stability owing to the susceptibility of ultrathin 2D membranes to the ambience [13-17]. Additionally, previous studies on valley quantum coherence are mainly limited to the wavelength range from the visible to the mid-infrared light [10-19], which cannot satisfy the applications in some far-infrared quantum information technologies [20,21].

The nanoscale hyperbolic shear phenomenon was discovered in the low-symmetry Bravais crystal  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, and the conception of hyperbolic shear polaritons (HShPs) was proposed as a class of polariton modes [22]. The HShPs originate from the monoclinic crystal structure of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>

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with nonorthogonal principal crystal axes, which have great potential in creating an anisotropic environment near the valleytronic material for exciting the coherence between two valleys at room temperature. The HShPs appear in the midto far-infrared region, which have preliminarily shown great promise for remarkably enhancing the near-field thermal radiation and the photonic spin Hall effect [23,24]. Monoclinic CdWO<sub>4</sub> crystal has also been demonstrated to support HShPs in a wide infrared range of  $200-900 \text{ cm}^{-1}$  [25]. The HShPs have sparked strong research interest due to their intriguing physicochemical characteristics [26–28]. Nevertheless, the study on HShPs is still in the prototype stage, and lots of research areas including the interplay between valley quantum coherence and HShPs have not yet been explored. There remain many open questions to be resolved. For instance, what discrepancies are there between the valley quantum interferences modulated by monoclinic Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> crystals? How do the valley quantum interference fringes evolve with various controlling factors such as the electron-doping concentration in monoclinic crystals, the thickness of monoclinic crystals, the azimuth and twist angles of monoclinic hybrid structures?

Inspired by the advances in valleytronics and hyperbolic polaritons, in this paper, we theoretically propose an approach to modify the valley quantum interference in the mid- to far-infrared spectral region. The discrepancies between the valley quantum interferences tuned by monoclinic Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> crystals as well as the evolutions of valley quantum interferences with the electron-doping concentration, crystal thickness, and azimuth and twist angles are clearly uncovered. The influencing mechanism of HShPs on the valley quantum interference is discussed in detail.

#### **II. MODEL AND THEORETICAL METHODS**

There are generally two strategies to generate the quantum coherence between two valley excitons. One involves an external coherent electromagnetic pump [9,29], and another one is spontaneous via generating an anisotropic environment in the vicinity of valley excitons [17,18]. The latter is relatively less explored and is the subject of this paper. In the mid- to far-infrared range, biased bilayer graphene [30] and photoexcited TMDCs [31,32] could serve as an important excitonic building block. The inset in Fig. 1(a) sketches two degenerate valleys K and K' in the electronic band structure of a hypothetical 2D valley material. Excitons in the K and K' valleys are coupled to photons with the helicities  $\sigma_{\pm}$ , respectively. We assume that one electron is initially excited to the lowest level of the conduction band of the K valley. In an isotropic electromagnetic vacuum, such as the case with free space, this excited electron returns to the ground state (i.e., the highest level of the valence band) via emitting a photon without exciting the orthogonal K' valley electron. However, in the presence of a neighboring monoclinic crystal material which creates a local in-plane anisotropic space near the valley material, the emission from the K valley can radiatively excite the electron in the K' valley and vice versa. Such coupling interaction leads to the spontaneous generation of valley coherence and yields quantum interference among their emissions [16–18].



FIG. 1. (a) A schematic of hyperbolic shear polariton (HShP)modulated valley quantum interference in a two-dimensional (2D) valley material. Crystal1 (or crystal2) stands for monoclinic Ga2O3 or CdWO<sub>4</sub> crystal. Monoclinic crystal1 and crystal2 create a local in-plane anisotropic environment which allows a finite nonzero coupling between mutually orthogonal valley excitons (see the inset) in the 2D valley material. The emission from the K valley with  $\sigma_+$ polarization can radiatively excite the orthogonal K' valley with  $\sigma_{-}$ polarization. Such interaction leads to the spontaneous generation of valley coherence and yields quantum interference among their emissions. Unit cells of (b) Ga<sub>2</sub>O<sub>3</sub> and (c) CdWO<sub>4</sub> with monoclinic angle  $\beta$  and the Cartesian coordinate system (x, y, z) fixed to the unit cells. (d) Schematic view from the top of the twist-induced monoclinic crystals. The surface of Ga<sub>2</sub>O<sub>3</sub> or CdWO<sub>4</sub> is the monoclinic (010) plane (x-y plane). The azimuth angle  $\Phi$  (or  $\Phi'$ ) of crystal1 (or crystal2) is the angle between the  $x_0$  and **a** axes, where  $(x_0, y_0, z_0)$  is the laboratory coordinate system. The twist angle between crystal1 and crystal2 is  $\theta = \Phi' - \Phi$ .

As shown in Fig. 1(a), the 2D valley material is placed above the stacked monoclinic crystal1 and crystal2. Crystal1 (or crystal2) can be monoclinic Ga<sub>2</sub>O<sub>3</sub> or CdWO<sub>4</sub> crystal. The factors  $d_g$ ,  $d_1$ , and  $d_2$  stand for the vertical distance of valley excitons from the surface of crystal1 and the thicknesses of crystal1 and crystal2, respectively. The valley material film is parallel to the monoclinic (010) plane (*x*-*y* plane) of crystal1 and crystal2. Since the literature still lacks specific expressions of dipole moments for two orthogonal far-infrared excitons in gapped Dirac systems, in our model, the following dipole moments which are suitable for two nontrivial tilted circular orthogonal dipoles in an *H*-type MoSe<sub>2</sub>/WSe<sub>2</sub> bilayer heterostructure are utilized [18]:

$$\mathbf{D}_{1} = (0.18 + 0.64i)\hat{\mathbf{x}} + (0.58 - 0.01i)\hat{\mathbf{y}} + (0.37 - 0.3i)\hat{\mathbf{z}},$$
(1)

$$\mathbf{D}_2 = (0.53 - 0.35i)\hat{\mathbf{x}} + (0.02 - 0.45i)\hat{\mathbf{y}} + (0.47 + 0.42i)\hat{z}.$$
(2)

In theory, any photonic environment which creates an anisotropy in the spontaneous emission rates in  $D_1$  and  $D_2$  directions will result in the coupling between these two valleys, thus leading to a finite generation of spontaneous valley coherence. The valley coherence can be quantified experimentally by a metric called the degree of linear polarization

(DoLP) of the emission with DoLP =  $(I_1-I_2)/(I_1 + I_2)$ . The symbols  $I_1$  and  $I_2$  are the intensities of two linearly polarized emissions. The steady-state DoLP in the absence of pumping is an ill-defined quantity as the populations in K(K') and valley coherence converge to zero [17]. To measure the spontaneous coherence, we posit a weak incoherent bidirectional pump. In this case, the DoLP is approximately equal to the valley quantum interference that is calculated by [16,17]

$$Q = (\Gamma_1 - \Gamma_2)/(\Gamma_1 + \Gamma_2), \qquad (3)$$

where  $\Gamma_1$  and  $\Gamma_2$  are the spontaneous emission rates for dipoles oriented along  $\mathbf{D}_1$  and  $\mathbf{D}_2$  directions, respectively. The spontaneous emission rate of an arbitrarily oriented emitter located nearby the anisotropic material can be derived from the Purcell factor that is given by [33,34]

$$F_p = \frac{\Gamma_{1,2}}{\Gamma_0} = 1 + \frac{6\pi c}{\omega} (\boldsymbol{\mu}_{1,2}^* \cdot \operatorname{Im}[\overline{\overline{G}}_s(\boldsymbol{r}_0, \boldsymbol{r}_0, \omega)] \cdot \boldsymbol{\mu}_{1,2}), \quad (4)$$

where  $\Gamma_0$  is the spontaneous emission rate in free space, *c* is the speed of light in vacuum,  $\omega$  is the angular frequency of the electromagnetic wave,  $\mu_{1,2}$  is the unit vector in the direction of the dipole moment of emitter,  $\overline{\overline{G}}_s(\mathbf{r}_0, \mathbf{r}_0, \omega)$  is the scattering part of dyadic Green function at the position of the dipole considering the presence of monoclinic crystals, and  $\mathbf{r}_0$  is the source position. Following the procedure outlined

in Refs. [33,34], the scattered-tensor Green's function at the source position can be calculated by

$$\overline{G}_{s}(\mathbf{r}_{0}, \mathbf{r}_{0}, \omega) = \frac{i}{8\pi^{2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (r_{ss}\overline{\overline{M}}_{ss} + r_{sp}\overline{\overline{M}}_{sp} + r_{ps}\overline{\overline{M}}_{ps} + r_{pp}\overline{\overline{M}}_{pp}) \times \exp(2ik_{z}z_{0})dk_{x}dk_{y}.$$
(5)

Here,  $r_{ij}$  (i, j = s, p) are the matrix elements of the tensor Fresnel reflection coefficient related to the incident s- and p-polarized light. The first and second letters of the subscript in each coefficient denote the polarization states of incident and reflected waves, respectively. The factors  $k_x$ ,  $k_y$ , and  $k_z$  are the components of wave vector along x, y, and z directions, respectively,  $z_0 = d_g$  is the distance between the monoclinic crystal and the emitter. The generalized  $4 \times 4$  transfer matrix formalism, which is capable of calculating the Fresnel coefficients and the field intensity distribution for light propagation in anisotropic stratified media [35,36], was utilized to theoretically explain the observed HShPs in experiment [22]. Thus, the generalized  $4 \times 4$  transfer matrix formalism is used to calculate the reflection coefficients  $r_{ij}$  here. The matrices  $\overline{M}_{ij}$  (*i*, *j* = *s*, *p*) in Eq. (5) are obtained by the following expressions [16,33,34]:

$$\overline{\overline{M}}_{ss} = \frac{1}{k_z k_\rho^2} \begin{pmatrix} k_y^2 & -k_x k_y & 0\\ -k_x k_y & k_y^2 & 0\\ 0 & 0 & 0 \end{pmatrix}, \quad \overline{\overline{M}}_{sp} = \frac{1}{k_0 k_\rho^2} \begin{pmatrix} -k_x k_y & -k_y^2 & -\frac{k_y k_\rho^2}{k_z} \\ k_x^2 & k_x k_y & \frac{k_x k_\rho^2}{k_z} \\ 0 & 0 & 0 \end{pmatrix},$$

$$\overline{\overline{M}}_{ps} = \frac{1}{k_0 k_\rho^2} \begin{pmatrix} k_x k_y & -k_x^2 & 0\\ k_y^2 & -k_x k_y & 0\\ -\frac{k_y k_\rho^2}{k_z} & \frac{k_x k_\rho^2}{k_z} & 0 \end{pmatrix}, \quad \overline{\overline{M}}_{pp} = \frac{k_z}{k_0^2 k_\rho^2} \begin{pmatrix} -k_x^2 & -k_x k_y & -\frac{k_y k_\rho^2}{k_z} \\ -k_x k_y & -k_y^2 & -\frac{k_y k_\rho^2}{k_z} \\ \frac{k_x k_\rho^2}{k_z} & \frac{k_y k_\rho^2}{k_z} & \frac{k_\rho k_\rho^2}{k_z} \end{pmatrix}, \quad (6)$$

where  $k_0 = (k_x^2 + k_y^2 + k_z^2)^{1/2}$  is the free-space wave vector and  $k_\rho = (k_x^2 + k_y^2)^{1/2}$  is the in-plane wave vector.

Monoclinic crystals are characterized by unequal lengths of their three principal axes and one shear angle. They support only the twofold axis of rotational symmetry along b and a mirror plane (a-c plane). Here, the parameters a, b, and c denote vectors of the unit cell, as shown in Figs. 1(b) and 1(c). Due to the monoclinic angle ( $\beta = 103.7^{\circ}$  and 91.13° for Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub>, respectively) [37,38], axes **a** and **c** are not perpendicular to each other. In view of the low crystal symmetry, the off-diagonal permittivity components cannot be completely removed through the coordinate rotation. Hence, four independent components of the permittivity tensor arise in monoclinic Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> crystals, written in Cartesian coordinates as  $\overline{\overline{\varepsilon}} = [\varepsilon_{xx} \ \varepsilon_{xy} \ 0; \ \varepsilon_{yx} \ \varepsilon_{yy} \ 0; \ 0 \ 0 \ \varepsilon_{zz}] \ (\varepsilon_{xy} =$  $\varepsilon_{yx}$  is bounded by reciprocity). Since all four components are complex-valued entries, the monoclinic permittivity tensor is a non-Hermitian tensor, and it is composed of the highfrequency contributions and the dipole charge resonances [25,37,38]. To unveil the influence of free charge carriers on the valley quantum interference, the doped monoclinic Ga<sub>2</sub>O<sub>3</sub> crystals with four free charge-carrier densities N (in cm<sup>-3</sup>) at  $\log_{10}N = 18.0$ , 18.5, 19.0, and 19.5 are also inspected in addition to the pure monoclinic Ga<sub>2</sub>O<sub>3</sub> crystal. The detailed calculation equations of permittivity tensors for monoclinic Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> crystals are given in Eqs. (S1)–(S7) in the Supplemental Material [39].

Generally, hyperbolic polaritons can be generated when either the real parts of two diagonal permittivity elements are negative and another one is positive or one is negative and two are positive. However, the strong dielectric response of offdiagonal terms  $\varepsilon_{xy} = \varepsilon_{yx} \neq 0$  in monoclinic crystals typically prevents the electromagnetic propagation angle from being aligned with the principal axes, inducing a prominent shearing effect of polariton modes. This shear phenomenon in the dielectric response leads to the appearance of so-called HShPs, where both momentum (wavelength) and propagation direction disperse with the frequency [22,25]. Figure 2 presents the real parts of permittivity elements, i.e.,  $\text{Re}(\varepsilon_{xx})$ ,  $\text{Re}(\varepsilon_{yy})$ ,  $\text{Re}(\varepsilon_{yy})$ , and  $\text{Re}(\varepsilon_{zz})$ , for monoclinic Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub>



FIG. 2. Real parts of permittivity elements for pure monoclinic (a)  $Ga_2O_3$  and (f) CdWO<sub>4</sub> crystals, and *n*-type doped  $Ga_2O_3$  crystals with (b)  $log_{10}N = 18.0$ , (c)  $log_{10}N = 18.5$ , (d)  $log_{10}N = 19.0$ , and (e)  $log_{10}N = 19.5$ . The wavelength ranges in which  $Re(\varepsilon_{xx})$ ,  $Re(\varepsilon_{yy})$ , and  $Re(\varepsilon_{zz})$  have different signs are shaded by different colors, and the corresponding signs of each color are shown in the left table.

crystals. Their corresponding imaginary parts of permittivity elements are given in Fig. S1 in the Supplemental Material [39].

The hyperbolic dispersion bands in which  $\text{Re}(\varepsilon_{xx})$ ,  $\text{Re}(\varepsilon_{xy})$ ,  $\text{Re}(\varepsilon_{yy})$ , and  $\text{Re}(\varepsilon_{zz})$  have opposite signs are shaded by 13 different colorful backgrounds. Depending on the combination of positive or negative real parts of four permittivity elements, various types of phonon polaritons are supported, such as elliptical surface phonon polaritons in green, type-I (in-plane in magenta and dusty blue, out-of-plane in light navy) and type-II (in-plane in wine, out-of-plane in orange) hyperbolic polariton modes.

By virtue of the low-symmetry lattice structure, one can also engineer the valley quantum interference via tuning the parameters of azimuth and twist angles. The azimuth angle  $\Phi$ (or  $\Phi'$ ) is defined by a certain in-plane rotation with respect to the normal of monoclinic crystal. That is, we tune the rotation angles  $\Phi$  and  $\Phi'$  of crystal1 and crystal2 around the  $z_0$  axis in-plane, as indicated in Figs. 1(a) and 1(d). Accordingly, the twist angle  $\theta$  is defined as  $\theta = \Phi' - \Phi$  [see Fig. 1(d)].

To make the valley excitons efficiently couple to the shear polaritons in monoclinic crystals, the position of valley exciton should be sufficiently far from the surface of monoclinic crystals such that it sees the crystals rather than several adjacent atoms. Nevertheless, the farther the valley exciton is, the larger the size of monoclinic crystal is required. The lattice constants of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (or CdWO<sub>4</sub>) are a = 12.23 Å, b = 3.04 Å, and c = 5.80 Å [37] (or a = 4.959 Å, b = 5.812 Å, and c = 5.020 Å) [38]. Especially valley excitons could suffer from the nonlocal effects induced via monoclinic crystals for only several nanometers of distance  $d_g$ . Figure S2 in the Supplemental Material [39] presents the variations of Purcell factors with respect to the wavelength  $\lambda$  and the distance  $d_g$  for dipoles oriented along **D**<sub>1</sub> and **D**<sub>2</sub> directions, respectively. One can see that the Purcell factors tend to be constants when the distance  $d_g$  increases to ~50 nm. Considering these, the vertical distance of valley excitons from the surface of crystal1 is taken to be  $d_g = 50$  nm.

### **III. RESULTS AND DISCUSSIONS**

We first consider the condition that crystal1 and crystal2 are the same monoclinic crystal and the twist angle  $\theta = 0^{\circ}$ (see Figs. 3–6 and S2–S9 in the Supplemental Material [39]). Figure S3 in the Supplemental Material [39] exhibits the colormaps of quantum interference Q vs the wavelength  $\lambda$  and the thickness  $d = d_1 + d_2$  when the azimuth angle  $\Phi = 90^{\circ}$ . It is found that the Q spectra present local minimum and



FIG. 3. (a) Real and (b) imaginary parts of Fresnel reflection coefficient  $r_{pp}$  for pure monoclinic Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> crystals, and doped Ga<sub>2</sub>O<sub>3</sub> crystals at different free charge-carrier densities. Quantum interferences (*Q*) for two orthogonal dipoles positioned at a distant height from the monoclinic Ga<sub>2</sub>O<sub>3</sub> crystal with (c) N = 0.0, (d)  $\log_{10}N = 18.0$ , (e)  $\log_{10}N = 18.5$ , (f)  $\log_{10}N = 19.0$ , (g)  $\log_{10}N = 19.5$ , and (h) pure CdWO<sub>4</sub> crystal. For comparison, their respective spectral curves of Im( $r_{pp}$ ) are replotted by white solid lines in (c)–(h).

maximum values around  $d = 8 \mu m$ . Thus, unless otherwise specified, the thicknesses of crystal1 and crystal2 are set to be  $d_1 = d_2 = 4.0 \mu m$  by default.

Figures 3(a) and 3(b) show the optical spectra of real and imaginary parts [i.e.,  $\operatorname{Re}(r_{pp})$  and  $\operatorname{Im}(r_{pp})$ ] of Fresnel reflection coefficient  $r_{pp}$ , respectively, when both the stacked crystal1 and crystal2 are monoclinic Ga2O3 (or CdWO4) crystal at  $\Phi = 90^{\circ}$ . Their corresponding quantum interferences Q for two orthogonal dipoles are plotted as a function of the wavelength  $\lambda$  in Figs. 3(c)–3(h). One can see that the variation tendency of quantum interference fringes is like that of the extreme values in  $Im(r_{pp})$  (cf. the white solid lines and the Q spectra). For the pure monoclinic crystals, as shown in Figs. 3(c) and 3(h), the wavelength positions of local minima (or maxima) of Q are slightly deviated from the dips (or peaks) of  $Im(r_{pp})$  spectra. For example, the Q spectral band in Fig. 3(c) for pure  $Ga_2O_3$  crystal presents the strongest negative (or positive) quantum interference at 30.5 µm (or 32.6  $\mu$ m), while its corresponding Im( $r_{pp}$ ) shows a dip (or peak) at 30.0  $\mu$ m (or 33.2  $\mu$ m). The Q spectral band in Fig. 3(h) for pure CdWO<sub>4</sub> crystal exhibits the smallest (or largest) quantum interference value at 24.5 µm (or 27.1 µm), while its corresponding  $Im(r_{pp})$  gives a dip (or peak) at 24.3  $\mu$ m (or 28.2  $\mu$ m). For the doped Ga<sub>2</sub>O<sub>3</sub> crystals, especially for  $\log_{10}N \ge 18.5$  in Figs. 3(e)–3(g), the spectral shape including the peak and dip positions of Q matches very well with that of  $Im(r_{pp})$ . Furthermore, the Q value region changes from -0.7 to 1.0 for pure monoclinic Ga<sub>2</sub>O<sub>3</sub> crystal [see Fig. 3(c)]. By contrast, the valley quantum interferences in Figs. 3(d)-3(g) become completely negative values after the  $Ga_2O_3$  crystal is doped by free charge carriers.

The imaginary part  $Im(r_{pp})$  is proportional to the photonic local density of states [40-42]. As the doping concentration N increases in monoclinic Ga<sub>2</sub>O<sub>3</sub>, the values of dips in  $\text{Im}(r_{pp})$ spectra mainly present an increased tendency, while that of the main peaks in  $Im(r_{pp})$  show a decreased trend, as depicted in Fig. 3(b). The dips in  $Im(r_{pp})$  gradually shift toward short wavelengths with increasing the N value. When the doping concentration increases to  $\log_{10}N = 19.0$  and 19.5, many dips and peaks disappear, and the  $Im(r_{pp})$  spectra become relatively flat, indicating the low sensitivity of photonic local density of states to the change of wavelength. In consequence, the quantum interference bands are gradually broadened, the dips in Q spectra exhibit blueshift, and Q is limited to a smaller and smaller negative value range with increasing the doping concentration [see Figs. 3(c)-3(g)]. In the later discussions on the optical field distributions, we will see that the decrease in color scales of Q spectra is also associated with the optical losses induced via electron doping.

For the pure Ga<sub>2</sub>O<sub>3</sub> crystal, the Re( $r_{pp}$ ) spectrum also shows a multipeak oscillation behavior [see Fig. 3(a)]. The Re( $r_{pp}$ ) gives its smallest value at  $\lambda = 32.7 \,\mu\text{m}$  which is very close to the wavelength position (32.6  $\mu\text{m}$ ) of maximum positive quantum interference in Fig. 3(c). This implies that the influence of Re( $r_{pp}$ ) on the Q spectra cannot be ignored for pure monoclinic crystals. By right of the impact of Re( $r_{pp}$ ), the wavelength positions of local minima (or maxima) of Qslightly stray from the dips (or peaks) of Im( $r_{pp}$ ) spectrum. Similarly, Re( $r_{pp}$ ) of pure CdWO<sub>4</sub> crystal gives its smallest dip value at 26.8  $\mu$ m, leading the largest peak at 27.1  $\mu$ m in Q spectrum to deviate from the position (at 28.2  $\mu$ m) of the strongest peak in Im( $r_{pp}$ ), as shown in Fig. 3(h). The dips



FIG. 4. Isofrequency surfaces for pure monoclinic (a)  $Ga_2O_3$  and (f) CdWO<sub>4</sub> crystals at the work wavelengths  $\lambda = 30.5$  and 24.5 µm, respectively. (b)–(e) are the isofrequency surfaces for doped  $Ga_2O_3$  crystals at electron-doping concentrations  $log_{10}N = 18.0$ , 18.5, 19.0, and 19.5, respectively. Their corresponding work wavelengths are  $\lambda = 30.0$ , 28.8, 28.6, and 28.3 µm, respectively. The red and blue surfaces denote the positive and negative signs of  $k_z/k_0$ . The contour lines at the bottom of each subgraph are the projections of isofrequency surfaces.

and peaks in  $\text{Re}(r_{pp})$  become increasingly weaker, even some of them disappear, as the doping concentration increases. The spectral shape of Q is little affected via the  $\text{Re}(r_{pp})$  such that it well coincides with that of  $\text{Im}(r_{pp})$  at high electron-doping concentrations.

The variation of valley quantum interference with Fresnel reflection coefficient in Fig. 3 can be further attributed to the evolution of dispersion bands of HShPs induced via electron doping in monoclinic  $Ga_2O_3$ . As show in Fig. 2, there are 11 kinds of color shades for pure monoclinic Ga<sub>2</sub>O<sub>3</sub>. The types of hyperbolic dispersion gradually decrease to be six kinds as the doping concentration increases to  $\log_{10}N = 19.5$ . The decrease of hyperbolic types is accompanied by the blueshifts and broadening of some dispersion bands (e.g., the dispersion bands shaded by dark cyan, orange, and green colors). As a result, many quantum interference fringes in Figs. 3(c)-3(g)shift toward the short wavelengths, even some weak quantum interference dips and peaks are gradually smeared out with increasing the doping concentration from  $\log_{10}N = 18.0$  to 19.5. There are only nine kinds of color shades for pure monoclinic CdWO<sub>4</sub> [see Fig. 2(f)]. Therefore, the quantum interference fringes modulated by CdWO<sub>4</sub> in Fig. 3(h) are less than those modified via  $Ga_2O_3$  in Fig. 3(c).

To more clearly unveil the underlying influencing mechanism of hyperbolic responses on the valley quantum interference, Figs. 4(a)–4(f) exemplifies the solutions for shear polariton wavevectors at  $\lambda = 30.5, 30.0, 28.8, 28.6, 28.3,$  and 24.5 µm for Ga<sub>2</sub>O<sub>3</sub> crystal with  $N = 0.0, \log_{10}N = 18.0,$ 18.5, 19.0, 19.5, and pure CdWO<sub>4</sub> crystal, respectively. These adopted  $\lambda$  values for Ga<sub>2</sub>O<sub>3</sub> correspond to the quantum interference dips at ~30 µm in Figs. 3(c)–3(g). Their discrepancies are the blueshifts induced by different concentrations of electron doping in  $Ga_2O_3$ . The solution method for Fig. 4 is described in Sec. 2 in the Supplemental Material [39].

One can see from Figs. 4(a)-4(e), when we change the doping concentrations in Ga<sub>2</sub>O<sub>3</sub> crystal, not only does the polariton wave vector magnitude change, but the direction of hyperboloid also rotates within the monoclinic plane. This is a typical feature of the reduced symmetry associated with HShPs supported in monoclinic crystals. For the pure crystals, both Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> possess the in-plane hyperbolic polariton mode, as shown in Figs. 4(a) and 4(f). After doping with  $\log_{10}N = 18.0$ , the isofrequency surface of  $Ga_2O_3$ crystal transits to the type-I out-of-plane HShP mode with two degeneracy points [see Fig. 4(b)]. Further increasing the doping concentration to  $\log_{10}N = 18.5$  [see Fig. 4(c)], the hyperbolic isofrequency surface undergoes compressing along both  $k_x$  and  $k_y$  axes. Meanwhile, the degeneracy points disappear, and there is only one vertex in the one-branched hyperboloid. As the doping concentration increases to  $log_{10}N =$ 19.0 and 19.5, the isofrequency surfaces transit to the in-plane hyperbolic topologies with different wave vector magnitudes and directions, as presented in Figs. 4(d) and 4(e).

Additionally, we also inspect the evolution of isofrequency surface with the electron-doping concentration at a fixed wavelength  $\lambda = 29.0 \,\mu\text{m}$ , as shown in Fig. S4 in the Supplemental Material [39]. In this case, all the Ga<sub>2</sub>O<sub>3</sub> crystals with N= 0.0, log<sub>10</sub>N = 18.0 and 18.5 support type-I out-of-plane HShP mode (see Figs. S4(a)–S4(c) in the Supplemental Material [39]). With increasing the doping concentration in Ga<sub>2</sub>O<sub>3</sub> crystal from log<sub>10</sub>N = 19.0 to 19.5 (Figs. S4(d) and S4(e) in the Supplemental Material [39]), we



FIG. 5. Variations of quantum interference Q with respect to the wavelength  $\lambda$  and the azimuth angle  $\Phi$ . The radial axis and angle stand for the factors of  $\lambda$  in  $\mu$ m and  $\Phi$  in degrees, respectively. (a) and (f) are for the cases of pure monoclinic Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> crystals, respectively. (b)–(e) are for the conditions of doped Ga<sub>2</sub>O<sub>3</sub> crystals with log<sub>10</sub>N = 18.0, 18.5, 19.0, and 19.5, respectively.

observe an optical topological transition from open (in-plane hyperbolic) to closed (elliptical) isofrequency surfaces. These rich topological transitions of shear polariton modes account for the blueshifts of quantum interference dips (even the broadening of interference bands and the disappearance of some fringes) at  $\sim$ 30 µm induced via increasing the doping concentrations in Ga<sub>2</sub>O<sub>3</sub> crystal.

The optical field distributions with respect to the excitation wavelength  $\lambda$  and  $z_0$  position for the conditions of Figs. 3(c)– 3(h) are shown in Figs. S5(a)-S5(f) in the Supplemental Material [39]. We see from Fig. S5 in the Supplemental Material [39] that the reflected light field as well as the optical field in monoclinic crystals mainly exhibits a diminished tendency with increasing the electron-doping concentration in Ga2O3 crystal, which is detrimental to the strengthening of valley quantum interference. This characteristic can be attributed to the influences of crystal losses on the HShPs. As depicted in Fig. S1 in the Supplemental Material [39], the imaginary parts of permittivity elements for Ga<sub>2</sub>O<sub>3</sub> crystal gradually increase with increasing the N values, which can cause the increment of electromagnetic wave absorption and convert more wave energy into the heat. Figure S6 in the Supplemental Material [39] shows the isofrequency surfaces of pure and doped monoclinic crystals after artificially setting all the imaginary parts of four permittivity elements to be zero. By comparing Fig. S6 in the Supplemental Material [39] with Fig. 4, it is found that the lossless makes the isofrequency surfaces smoother and the losses limit the effective transmission of electromagnetic wave through monoclinic crystals. Hereby, the variation amplitude of Fresnel reflection coefficient becomes weaker and weaker with increasing the doping concentration, as shown in Figs. 3(a) and 3(b). Accordingly, the Q spectra in Fig. 3 along with Fig. 5 are gradually limited to a smaller and smaller negative value range as the doping concentration increases in the monoclinic crystal.

Figures 5(a)–5(f) exhibit the colormaps of quantum interference Q vs the wavelength  $\lambda$  and the azimuth angle  $\Phi$  for different doping concentrations of Ga<sub>2</sub>O<sub>3</sub> and pure CdWO<sub>4</sub> crystals. Their corresponding optical spectra of Im( $r_{pp}$ ) are shown in Figs. S7(a)–S7(f) in the Supplemental Material [39]. Because the origin of polar coordinate stands for  $\lambda = 0.0 \,\mu\text{m}$ and the wavelength range  $\lambda < 18 \,\mu\text{m}$  is beyond the scope of this paper, all the central results of polar coordinates in this paper are blank. The optical field distributions  $|E_x|$  as a function of  $z_0$  position at four different azimuth angles are given in Figs. S8(a)–S8(f) in the Supplemental Material [39]. All the azimuthal dispersions of Q, Im $(r_{pp})$ , and  $|E_x|$ exhibit no mirror symmetry about the crystal axes. In marked contrast, after artificially setting the off-diagonal permittivity element  $\varepsilon_{xy}$  to be zero, as shown in Fig. S9 in the Supplemental Material [39], the optical spectra of Q, Im $(r_{pp})$ , and  $|E_x|$  become symmetric about the crystal axes  $\Phi = 0^{\circ}$  (180°) and 90°. This phenomenon delineates the effects of symmetry breaking of monoclinic crystal structure in the valley quantum interference.

This broken symmetry also endows the valley quantum interference with exclusive azimuthal-dispersion property. In Fig. 5, the azimuth angles of interference fringes rotate with tunning the doping concentration in monoclinic crystals. For example, the Q spectrum in Fig. 5(a) for pure Ga<sub>2</sub>O<sub>3</sub> crystal presents a local minimum value at the coordinate  $(\lambda, \Phi)$ =  $(30.5 \,\mu\text{m}, 90^\circ)$ . As the doping concentration increases to  $\log_{10}N = 18.0, 18.5, 19.0, 19.5$ , the corresponding local minimum value shifts to  $(30.0 \,\mu\text{m}, 80^\circ)$ ,  $(28.8 \,\mu\text{m}, 142^\circ)$ ,  $(28.2 \,\mu\text{m}, 142^\circ)$ 136°), and (28.1  $\mu$ m, 140°), respectively. Based on the above discussions, the change of  $\lambda$  value is mainly attributed to the shift of hyperbolic dispersion band marked by cyan color in Fig. 2. As for the variation of the  $\Phi$  value, as depicted by open squares in Fig. 6(a), it could be ascribed to the change of lattice displacement direction (which can change the propagation direction of shear polaritons) within the monoclinic plane induced via tuning the doping concentration [43].

To further parameterize the rotation nature, the major polarizability angle is defined by

$$\alpha(\lambda) = \frac{1}{2} \arctan\left[\frac{2\operatorname{Re}(\varepsilon_{xy})(\lambda)}{\operatorname{Re}(\varepsilon_{xx})(\lambda) - \operatorname{Re}(\varepsilon_{yy})(\lambda)}\right], \quad (7)$$

which diagonalizes the real part of the permittivity tensor of monoclinic crystal individually at each wavelength. Figure 6(b) shows the dispersion curves of  $\alpha(\lambda)$  for pure monoclinic Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> crystals and doped Ga<sub>2</sub>O<sub>3</sub> crystals at different *N* values. The  $\alpha$  values at  $\lambda = 30.5$ , 30.0, 28.8, 28.2, and 28.1 µm are marked by solid squares for Ga<sub>2</sub>O<sub>3</sub> crystal with *N*= 0.0, log<sub>10</sub>*N* = 18.0, 18.5, 19.0, and 19.5, respectively. In Fig. 6(a), the  $\Phi$  values are nearly equal to the  $\alpha$  values (cf. the solid and open squares).



FIG. 6. (a) The azimuth and the major polarizability angles at which the quantum interferences Q have local maximum (see the circular symbols) and minimum (see the square symbols) values for pure (N = 0) monoclinic Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> crystals, and doped Ga<sub>2</sub>O<sub>3</sub> crystals. The solid lines are just drawn as a guide to the eye. (b) Dispersion curves of the major polarizability angle  $\alpha(\lambda)$  for pure monoclinic Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> crystals, and doped Ga<sub>2</sub>O<sub>3</sub> crystals at different *N* values. Solid (or open) circles indicate the  $\alpha$  (or  $\Phi$ ) values at  $\lambda = 34.6 \,\mu\text{m}$  for Ga<sub>2</sub>O<sub>3</sub> and  $\lambda = 26.8 \,\mu\text{m}$  for CdWO<sub>4</sub>. Solid (or open) squares indicate the  $\alpha$  (or  $\Phi$ ) values at  $\lambda = 30.5$ , 30.0, 28.8, 28.2, 28.1, and 24.4  $\mu\text{m}$  for Ga<sub>2</sub>O<sub>3</sub> crystal with N = 0.0,  $\log_{10}N = 18.0$ , 18.5, 19.0, 19.5, and pure CdWO<sub>4</sub> crystal, respectively.

Furthermore, open (or solid) circles in Fig. 6(a) present the  $\Phi$  (or  $\alpha$ ) values at  $\lambda = 34.6 \,\mu\text{m}$  for pure and doped Ga<sub>2</sub>O<sub>3</sub> crystals. The azimuth angle monotonically increases with increasing the doping concentration, in accordance with the variation of the major polarizability angle. At  $\lambda = 34.6 \,\mu\text{m}$ , because the hyperbolic polariton mode is nearly unchanged via the electron doping [always shaded by orange color, as shown in Figs. 2(a)–2(e)] and all the *Q* spectra in Figs. 5(a)–5(e) have local maximum values, this can eliminate the influences originating from the shift of hyperbolic dispersion band and the related change of polariton mode. Figure 6(a) clearly demonstrates that the propagation directional changes of shear polaritons parameterized by Eq. (7) are responsible for the azimuthal dispersion of valley quantum interference fringes in Fig. 5.

For the CdWO<sub>4</sub> crystal, the *Q* spectrum in Fig. 5(f) has local minimum and maximum values at (24.4 µm, 140°) and (26.8 µm, 56°), respectively. Their corresponding major polarizability angles are  $\alpha = 51^{\circ} + 90^{\circ}$  and 56°, respectively, as shown in Fig. 6. Here, the difference value 90° is the repetition period of wavelength-dependent major polarizability axes [22]. Again, it evidences that the azimuth and the major polarizability angles are approximately equal at the extreme values of *Q* spectra. This finding could be significant since it provides one strategy, i.e., through characterizing the valley quantum interference, to measure the lattice displacement direction and the doping concentration in monoclinic crystals.

Figures 7(a)–7(d) show the variations of quantum interference Q with respect to the wavelength  $\lambda$  and the twist angle  $\theta$  for the hybrid architectures of Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>-CdWO<sub>4</sub>, CdWO<sub>4</sub>-CdWO<sub>4</sub>, and CdWO<sub>4</sub>-Ga<sub>2</sub>O<sub>3</sub>. To more clearly distinguish the quantum interference fringes, the color scales of Q in Figs. 7(a)–7(d) are limited to a smaller



FIG. 7. Variations of quantum interference Q with respect to the wavelength  $\lambda$  and the twist angle  $\theta$  for the hybrid architectures of (a) Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub>, (b) Ga<sub>2</sub>O<sub>3</sub>-CdWO<sub>4</sub>, (c) CdWO<sub>4</sub>-CdWO<sub>4</sub>, and (d) CdWO<sub>4</sub>-Ga<sub>2</sub>O<sub>3</sub>. The radial axis and angle stand for the factors of  $\lambda$  in  $\mu$ m and  $\theta$  in degrees, respectively. The azimuth angle  $\Phi$  of crystal1 is tuned from 0° to 180°, while the azimuth angle  $\Phi'$  of crystal2 is fixed at 90°. Both Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> crystals are pure monoclinic crystals.

range. Original colormaps of Q are shown in Figs. S11(b), S11(f), S11(j), and S11(n) in the Supplemental Material [39]. The optical field distributions for these four hybrid structures as a function of the wavelength  $\lambda$  and  $z_0$  position at  $\theta = 0^{\circ}$ ,  $30^{\circ}$ ,  $60^{\circ}$ , and  $90^{\circ}$  are presented in Fig. S10 in the Supplemental Material [39]. Both Ga<sub>2</sub>O<sub>3</sub> and CdWO<sub>4</sub> crystals are pure monoclinic crystals in Figs. 7, S10, and S11 in the Supplemental Material [39].

In Fig. 7(a), two quantum interference fringes can be found near the  $\lambda = 32.5$  and 35 um around  $\theta = 0^{\circ}$  for the hybrid structure of Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub>. These two fringes mainly increase in interference intensity and gradually merge with increasing the twist angle up to 71°. Thereafter, they gradually disappear as the twist angle increases to  $90^{\circ}$ . This variation tendency is in conformity with the intensity change of reflected light field, as shown in Figs. S10(a)-S10(d) in the Supplemental Material [39]. At  $\theta = 0^{\circ}$ , the structure of Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub> gives rise to relatively strong reflected light fields at  $\sim$ 32.5 and  $\sim$ 35 µm (see Fig. S10(a) in the Supplemental Material [39]). As  $\theta$  increases to 30° and 60° (Figs. S10(b) and S10(c) in the Supplemental Material [39]), these two field intensity bands gradually merge into one at  $\sim$ 34 µm, and the intensity becomes stronger. When  $\theta$  increases to 90° (Fig. S10(d) in the Supplemental Material [39]), the field intensity at  $\sim$  34 µm is severely attenuated. At the same twist angle (cf. Figs. S10(a)–S10(d) and S10(e)–S10(h) in the Supplemental Material [39]), the reflected light fields at  $\sim$ 32.5 and  $\sim$ 35 µm for the structure of Ga<sub>2</sub>O<sub>3</sub>-CdWO<sub>4</sub> are stronger than those for Ga<sub>2</sub>O<sub>3</sub>-Ga<sub>2</sub>O<sub>3</sub>. Hereby, two strong quantum interference fringes can be clearly observed throughout the whole inspected  $\theta$  value region for the structure of Ga<sub>2</sub>O<sub>3</sub>-CdWO<sub>4</sub>, as shown in Fig. 7(b).

Similarly, the quantum interference fringes for the structures of CdWO<sub>4</sub>-CdWO<sub>4</sub> and CdWO<sub>4</sub>-Ga<sub>2</sub>O<sub>3</sub> are also determined via the reflected light field intensities. For instance, at  $\theta = 60^{\circ}$ , 90° and  $\lambda = 46.5 \,\mu\text{m}$  (cf. Figs. S10(k), S10(1), and S10(o), S10(p) in the Supplemental Material [39]), the reflected light field of CdWO<sub>4</sub>-Ga<sub>2</sub>O<sub>3</sub> is far larger than that of CdWO<sub>4</sub>-CdWO<sub>4</sub> such that there is (or no) a strong valley quantum interference fringe in Fig. 7(d) [or Fig. 7(c)] at 46.5  $\mu$ m with ranging the twist angle from 60° to 90°. After expanding the twist angle to  $-90^{\circ}$ , Figs. 7(a)–7(d) present four different symmetry-broken valley quantum interference patterns. Thus, in practical applications, the valley quantum interference could be utilized to estimate the stacking sequence and directions of multilayer monoclinic crystals.

Finally, Figs. S12(a) - S12(p) in the Supplemental Material [39] compare the quantum interference spectra for four hybrid architectures at different thickness ratios of  $d_1 = 0.5d_2$ ,  $d_1 =$  $2d_2$ , and  $d_1 = 3d_2$ . In each subgraph, the controlling factors, i.e., the radial axis and the radial angle, are the wavelength  $\lambda$ and the twist angle  $\theta$ . For better comparison, Figs. 7(a)-7(d) are repeated in Figs. S12(b), S12(f), S12(j), and S12(n) in the Supplemental Material [39], i.e., the condition of  $d_1 = d_2$ . The number of valley quantum interference fringes increases as the ratio  $d_1/d_2$  increases for the hybrid architectures of  $Ga_2O_3$ - $Ga_2O_3$  (see Figs. S12(a)-S12(d) in the Supplemental Material [39]) and Ga<sub>2</sub>O<sub>3</sub>-CdWO<sub>4</sub> (see Figs. S12(e)–S12(h) in the Supplemental Material [39]). This may originate from the fact that thicker monoclinic Ga<sub>2</sub>O<sub>3</sub> crystal by virtue of its shear effect creates a stronger anisotropic environment near the valley excitons. In marked contrast, the number of interference fringes decreases as the ratio  $d_1/d_2$  increases for the hybrid architecture of CdWO<sub>4</sub>-Ga<sub>2</sub>O<sub>3</sub> (see Figs. S12(m)-S12(p) in the Supplemental Material [39]). This is because the shear effect of CdWO<sub>4</sub> crystal is weaker than that of Ga<sub>2</sub>O<sub>3</sub> crystal. The thickening of monoclinic CdWO<sub>4</sub> as crystal1 will increase the distance between valley excitons and crystal2 (i.e., Ga<sub>2</sub>O<sub>3</sub> crystal), which is detrimental to valley quantum interference. For the case of CdWO<sub>4</sub>-CdWO<sub>4</sub> (see Figs. S12(i)–S12(l) in the Supplemental Material [39]), the interference fringes for  $d_1 = d_2$  are more than those for  $d_1 = 0.5d_2$ . At this condition, both crystall and crystal2 are monoclinic CdWO<sub>4</sub> such that increasing  $d_1$  can generate a stronger anisotropic environment near the valleytronic material. Nonetheless, the further increase of  $d_1$  will reduce the contribution from nonzero twist angle to the anisotropy of environment. Because of the weak shear effect, the thickening of CdWO<sub>4</sub> as crystal1 may not compensate the diminished contribution from nonzero twist angle. Thus, Figs. S12(k) and S12(1) in the Supplemental Material [39] exhibit different variation tendency from Figs. S12(c) and S12(d) in the Supplemental Material [39] for the case of  $Ga_2O_3$ - $Ga_2O_3$ . That is, the interference fringes for the case of CdWO<sub>4</sub>-CdWO<sub>4</sub> become less and less with increasing the thickness ratio to be  $d_1 = 2d_2$  and  $d_1 = 3d_2$ .

## **IV. CONCLUSIONS**

To summarize, we have discussed a spontaneous generation of valley quantum interference between two orthogonal dipoles in a 2D valleytronic material interfaced with stacked monoclinic  $Ga_2O_3$  and/or CdWO<sub>4</sub> crystals. Results show that the valley quantum interference can be broadly modulated in the mid- to far-infrared region using the shear polaritons in monoclinic crystals. Even so, CdWO<sub>4</sub> crystal only supports a weak shear effect stemming from the small monoclinic angle  $(91.13^{\circ})$  that limits the ability to fully quantify the behavior of shear polaritons. For Ga<sub>2</sub>O<sub>3</sub> crystal, this shear effect is significantly amplified as the monoclinic axis is offset at 103.7°. Consequently, the valley quantum interference fringes modulated by pure Ga<sub>2</sub>O<sub>3</sub> crystal are more than those tuned via pure CdWO<sub>4</sub> crystal. Additionally, the spectral shape of valley quantum interference Q is like that of  $Im(r_{pp})$ . Especially the sensitivity of photonic local density of states to the change of wavelength is gradually reduced with an increment of the electron-doping concentration in monoclinic crystals. Thus, the spectral shapes of Q and  $Im(r_{pp})$  are quite in accordance with each other at high doping concentrations. With increasing the doping concentrations in monoclinic Ga<sub>2</sub>O<sub>3</sub> crystal, the number of HShP modes gradually decreases accompanied by the blueshifts and broadening of some hyperbolic dispersion bands. As a result, many quantum interference fringes are widened and shift toward the short wavelengths. Moreover, the electron doping can increase the optical losses which limit the effective propagation of shear polaritons in monoclinic crystals. Hence, the valley quantum interference is gradually reduced to a smaller and smaller negative value range as the doping concentration increases in the Ga<sub>2</sub>O<sub>3</sub> crystal. In virtue of the azimuthal dispersion of HShPs propagation direction within the monoclinic plane, the quantum interference fringes change their directions with increasing the doping concentrations in monoclinic crystals. The valley quantum interference exhibits symmetry-broken patterns depending upon tuning the rotation angle and the twist angle of monoclinic hybrid structures around the z axis in the plane. This means that the valley quantum interference can be used to characterize the phonon modes and structural microvariations including the lattice displacement direction and the electron-doping concentration in monoclinic crystals. The findings also indicate that low-symmetry Bravais crystals can serve as prospective candidates for manipulating the spontaneous valley coherence in 2D valleytronic materials.

In experiment, the valley quantum coherence can be effectively detected and manipulated with polarization-resolved photoluminescence measurements [9–15]. It is worth noting that the dipole moments of valley excitons in a  $MoSe_2/WSe_2$  bilayer heterostructure are used here due to lack of specific expressions of dipole moments for orthogonal far-infrared excitons. These valley excitons may be formed at wavelengths away from the mode range of HShPs. As such, far-infrared valleytronic materials are needed to be developed in an actual experiment. Even so, the predicted physical phenomena as well as the revealed interplay mechanism between valley excitons and HShPs in this paper offer vistas and theoretical guidance for the future designing of active valleytronic quantum devices.

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- A. Pal, S. Zhang, T. Chavan, K. Agashiwala, C. H. Yeh, W. Cao, and K. Banerjee, Quantum-engineered devices based on 2D materials for next-generation information processing and storage, Adv. Mater. 35, 2109894 (2023).
- [2] S. A. Iyengar, A. B. Puthirath, and V. Swaminathan, Realizing quantum technologies in nanomaterials and nanoscience, Adv. Mater. 35, 2107839 (2023).
- [3] Y.-T. Fang, P. Gong, and F. Bu, Bound band in the continuum from merging of topological edge states and magnetic interface states, Opt. Laser Technol. **171**, 110309 (2024).
- [4] A. Ciarrocchi, F. Tagarelli, A. Avsar, and A. Kis, Excitonic devices with van der Waals heterostructures: Valleytronics meets twistronics, Nat. Rev. Mater. 7, 449 (2022).
- [5] S. Lai, Z. Zhang, N. Wang, A. Rasmita, Y. Deng, Z. Liu, and W. B. Gao, Dual-gate all-electrical valleytronic transistors, Nano Lett. 23, 192 (2023).
- [6] R. Li, P.-H. Fu, J.-F. Liu, and J. Wang, Armchair edge states in shear-strained graphene: Magnetic properties and quantum valley Hall edge states, Phys. Rev. B 109, 045403 (2024).
- [7] F. Langer, C. P. Schmid, S. Schlauderer, M. Gmitra, J. Fabian, P. Nagler, C. Schuller, T. Korn, P. G. Hawkins, J. T. Steiner *et al.*, Lightwave valleytronics in a monolayer of tungsten diselenide, Nature (London) 557, 76 (2018).
- [8] D. Ko, A. V. Morozov, V. M. Kovalev, and I. G. Savenko, Optical valleytronics of impurity states in two-dimensional Dirac materials, Phys. Rev. B 103, L161301 (2021).
- [9] A. M. Jones, H. Yu, N. J. Ghimire, S. Wu, G. Aivazian, J. S. Ross, B. Zhao, J. Yan, D. G. Mandrus, D. Xiao *et al.*, Optical generation of excitonic valley coherence in monolayer WSe<sub>2</sub>, Nat. Nanotechnol. 8, 634 (2013).
- [10] M. Xiang, J. Fu, C. Huang, Y. Xing, J. Zhang, H. Zeng, and X. Shao, Direct growth of monolayer WS<sub>2</sub> on rutile TiO<sub>2</sub> for enhanced valley coherence, J. Phys. Chem. C **127**, 7425 (2023).
- [11] F. Cadiz, S. Gerl, T. Taniguchi, and K. Watanabe, Imaging the effect of high photoexcited densities on valley polarization and coherence in MoS<sub>2</sub> monolayers, npj 2D Mater. Appl. 6, 27 (2022).
- [12] P. Herrmann, S. Klimmer, T. Lettau, M. Monfared, I. Staude, I. Paradisanos, U. Peschel, and G. Soavi, Nonlinear all-optical coherent generation and read-out of valleys in atomically thin semiconductors, Small 19, 2301126 (2023).
- [13] M. Khatoniar, N. Yama, A. Ghazaryan, S. Guddala, P. Ghaemi, K. Majumdar, and V. Menon, Optical manipulation of layer-valley coherence via strong exciton-photon coupling in microcavities, Adv. Opt. Mater. 11, 2202631 (2023).
- [14] C. Han and J. Ye, Polarized resonant emission of monolayer WS<sub>2</sub> coupled with plasmonic sawtooth nanoslit array, Nat. Commun. 11, 713 (2020).
- [15] L. Qiu, C. Chakraborty, S. Dhara, and A. N. Vamivakas, Roomtemperature valley coherence in a polaritonic system, Nat. Commun. 10, 1513 (2019).
- [16] A. Bapat, S. Dixit, Y. Gupta, T. Low, and A. Kumar, Gate tunable light-matter interaction in natural biaxial

hyperbolic van der Waals heterostructures, Nanophotonics **11**, 2329 (2022).

- [17] M. Nalabothula, P. K. Jha, T. Low, and A. Kumar, Engineering valley quantum interference in anisotropic van der Waals heterostructures, Phys. Rev. B 102, 045416 (2020).
- [18] M. Sohoni, P. K. Jha, M. Nalabothula, and A. Kumar, Interlayer exciton valleytronics in bilayer heterostructures interfaced with a phase gradient metasurface, Appl. Phys. Lett. **117**, 121101 (2020).
- [19] P. K. Jha, N. Shitrit, X. Ren, Y. Wang, and X. Zhang, Spontaneous exciton valley coherence in transition metal dichalcogenide monolayers interfaced with an anisotropic metasurface, *Phys. Rev. Lett.* **121**, 116102 (2018).
- [20] P. Stammer, J. Rivera-Dean, T. Lamprou, E. Pisanty, M. F. Ciappina, P. Tzallas, and M. Lewenstein, High photon number entangled states and coherent state superposition from the extreme ultraviolet to the far infrared, Phys. Rev. Lett. 128, 123603 (2022).
- [21] S. Chick, N. Stavrias, K. Saeedi, B. Redlich, P. T. Greenland, G. Matmon, M. Naftaly, C. R. Pidgeon, G. Aeppli, and B. N. Murdin, Coherent superpositions of three states for phosphorous donors in silicon prepared using THz radiation, Nat. Commun. 8, 16038 (2017).
- [22] N. C. Passler, X. Ni, G. Hu, J. R. Matson, G. Carini, M. Wolf, M. Schubert, A. Alù, J. D. Caldwell, T. G. Folland *et al.*, Hyperbolic shear polaritons in low-symmetry crystals, Nature (London) **602**, 595 (2022).
- [23] C.-L. Zhou, G. Tang, Y. Zhang, M. Antezza, and H.-L. Yi, Radiative heat transfer in a low-symmetry Bravais crystal, Phys. Rev. B 106, 155404 (2022).
- [24] G. Jia, W. Xue, Z. Jia, and M. Schubert, Giant photonic spin Hall effect induced by hyperbolic shear polaritons, Phys. Chem. Chem. Phys. 25, 11245 (2023).
- [25] G. Hu, W. Ma, D. Hu, J. Wu, C. Zheng, K. Liu, X. Zhang, X. Ni, J. Chen, X. Zhang *et al.*, Real-space nanoimaging of hyperbolic shear polaritons in a monoclinic crystal, Nat. Nanotechnol. 18, 64 (2023).
- [26] J. Matson, S. Wasserroth, X. Ni, M. Obst, K. Diaz-Granados, G. Carini, E. M. Renzi, E. Galiffi, T. G. Folland, L. M. Eng *et al.*, Controlling the propagation asymmetry of hyperbolic shear polaritons in beta-gallium oxide, Nat. Commun. 14, 5240 (2023).
- [27] C. Hu, T. Sun, Y. Zeng, W. Ma, Z. Dai, X. Yang, X. Zhang, and P. Li, Source-configured symmetry-broken hyperbolic polaritons, Elight 3, 14 (2023).
- [28] G. Jia, J. Luo, H. Wang, Q. Ma, Q. Liu, H. Dai, and R. Asgari, Two-dimensional natural hyperbolic materials: From polaritons modulation to applications, Nanoscale 14, 17096 (2022).
- [29] K. Hao, G. Moody, F. Wu, C. K. Dass, L. Xu, C.-H. Chen, L. Sun, M.-Y. Li, L.-J. Li, A. H. MacDonald *et al.*, Direct measurement of exciton valley coherence in monolayer WSe<sub>2</sub>, Nat. Phys. **12**, 677 (2016).

- [30] M. O. Sauer and T. G. Pedersen, Exciton absorption, band structure, and optical emission in biased bilayer graphene, Phys. Rev. B 105, 115416 (2022).
- [31] J. Madéo, M. K. L. Man, C. Sahoo, M. Campbell, V. Pareek, E. L. Wong, A. Al-Mahboob, N. S. Chan, A. Karmakar, B. M. K. Mariserla *et al.*, Directly visualizing the momentumforbidden dark excitons and their dynamics in atomically thin semiconductors, Science **370**, 1199 (2020).
- [32] D. Yagodkin, L. Nádvorník, O. Gueckstock, C. Gahl, T. Kampfrath, and K. I. Bolotin, Ultrafast photocurrents in MoSe<sub>2</sub> probed by terahertz spectroscopy, 2D Mater. 8, 025012 (2021).
- [33] L. Novotny and B. Hecht, *Principles of Nano-Optics* (Cambridge University Press, Cambridge, 2012).
- [34] B. Sikder, S. H. Nayem, and S. Z. Uddin, Deep ultraviolet spontaneous emission enhanced by layer dependent black phosphorus plasmonics, Opt. Express 30, 47152 (2022).
- [35] N. C. Passler and A. Paarmann, Generalized  $4 \times 4$  matrix formalism for light propagation in anisotropic stratified media: Study of surface phonon polaritons in polar dielectric heterostructures, J. Opt. Soc. Am. B **34**, 2128 (2017).
- [36] N. C. Passler and A. Paarmann, Generalized  $4 \times 4$  matrix formalism for light propagation in anisotropic stratified media: Study of surface phonon polaritons in polar dielectric heterostructures: Erratum, J. Opt. Soc. Am. B **36**, 3246 (2019).

- [37] M. Schubert, R. Korlacki, S. Knight, T. Hofmann, S. Schöche, V. Darakchieva, E. Janzén, B. Monemar, D. Gogova, Q. T. Thieu *et al.*, Anisotropy, phonon modes, and free charge carrier parameters in monoclinic β-gallium oxide single crystals, Phys. Rev. B **93**, 125209 (2016).
- [38] A. Mock, R. Korlacki, S. Knight, and M. Schubert, Anisotropy, phonon modes, and lattice anharmonicity from dielectric function tensor analysis of monoclinic cadmium tungstate, Phys. Rev. B 95, 165202 (2017).
- [39] See Supplemental Material at http://link.aps.org/supplemental/ 10.1103/PhysRevB.109.155417 for calculation methods of the permittivity tensors and of the isofrequency surfaces for monoclinic crystals, and Figs. S1–S12.
- [40] H. N. S. Krishnamoorthy, Z. Jacob, E. Narimanov, I. Kretzschmar, and V. M. Menon, Topological transitions in metamaterials, Science 336, 205 (2012).
- [41] Y. Hu, H. Liu, B. Yang, K. Shi, M. Antezza, X. Wu, and Y. Sun, High-rectification near-field radiative thermal diode using Weyl semimetals, Phys. Rev. Mater. 7, 035201 (2023).
- [42] H. Wu, Y. Huang, L. Cui, and K. Zhu, Active magneto-optical control of near-field radiative heat transfer between graphene sheets, Phys. Rev. Appl. 11, 054020 (2019).
- [43] M. Schubert, A. Mock, R. Korlacki, S. Knight, Z. Galazka, G. Wagner, V. Wheeler, M. Tadjer, K. Goto, and V. Darakchieva, Longitudinal phonon plasmon mode coupling in β-Ga<sub>2</sub>O<sub>3</sub>, Appl. Phys. Lett. **114**, 102102 (2019).