

Symmetry-related properties of plasmon-polaritons in binary metallic supercrystals with cubic structures

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We extend our theoretical description of optical excitations in binary plasmonic supercrystals made of two types of metal nanoparticles to three common cubic structures: sodium chloride (NaCl), zinc blende (ZnS), and auricupride (Cu₃Au). Our microscopic model of plasmon polaritons in supercrystals incorporates dipole and quadrupole nanoparticle excitations, their interactions, and their coupling with photons. We calculate the plasmon-polariton dispersion for the three cubic structures starting from the dipole and quadrupole energies obtained in the quasistatic approximation. The bands depend on the properties of the nanoparticles as well as the symmetry and the lattice parameters of the supercrystals. To gain further insight into the coupling of different excitations and develop a set of symmetry selection rules for each structure, we complement our calculations with an extensive group theory analysis. Comparing the results across various structures makes our symmetry analysis more general, enabling us to observe selection rules that apply to multiple structures.

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I. INTRODUCTION

Plasmonic nanoparticle supercrystals are promising artificial materials for tailoring exquisite optical properties that enable applications in analytical chemistry, bioimaging, thermal transport, optical coatings, and waveguiding [1–7]. They are three-dimensional self-assembled [8–10] arrays of metallic nanoparticles with long-range crystalline order. The excitation spectrum of plasmonic supercrystals is characterized by the formation of plasmon-polaritons. These hybrid light-matter states create a regular array of electromagnetic hot spots inside the supercrystals that may be used for plasmon-enhanced spectroscopy, analytics, and photocatalysis [2,3].

Light-matter coupling of supercrystal plasmon-polaritons is in the regime of ultrastrong coupling. This means that the coupling strength reaches a considerable fraction of the bare excitation frequency [11,12]. The resulting plasmon-polaritons are transverse collective excitations that propagate through the crystal. Their formation is independent of material losses that determine the lifetime of the polariton state together with radiative losses for finite crystal size. In thin slabs of supercrystals plasmon-polaritons form standing waves leading to optical resonances across a broad spectral range [1,13–15].

We developed a quantum description of plasmon polaritons in supercrystals, starting from the dipole and quadrupole excitations of the nanoparticles, their interaction, and their

coupling to photons. The model accurately predicts the optical excitations of supercrystals and aligns with experimental data [1] and numerical simulations based on finite difference methods [16]. In our previous work [17], we used it to simulate the first binary supercrystal structure with more than one nanoparticle in the primitive cell. We demonstrated that such superstructures provide a greater degree of freedom in tailoring the optical response by controlling a few key parameters, such as the size of the nanoparticles and their material composition. The bonding between the nanoparticles is facilitated via surface-terminating ligands, thereby rendering the material properties of the nanoparticles themselves inconsequential in the structure self-assembly process [8–10,18].

We employed group theory to obtain selection rules for the photon-plasmon interaction and to predict behaviors such as degeneracy and mixing of the dipole- and quadrupole-derived states. This demonstrated the dependence of the plasmon-polariton dispersion on the symmetry of the crystal structure. Polydisperse nanoparticles have the capacity to self-assemble into a wide variety of structures characterized by distinct symmetries [19–23]. In this study, we focused on the exploration of these symmetry-related properties by incorporating three novel binary cubic structures into our analytical framework.

This paper extends the microscopic description of binary plasmonic supercrystals to three common cubic lattices: sodium chloride (NaCl), zinc sulfide (ZnS), and auricupride (Cu₃Au). Each of these structures exhibits distinct symmetry features, leading to a deeper understanding of the principles governing matter-matter and light-matter interactions. For a chosen set of material parameters, we calculate the dispersion of all optical excitations for each new structure. As in our previous work, we assemble group theory tables listing the symmetries of these excitations and devise selection rules guiding such behaviors as degeneracy. The incorporation of

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TABLE I. An overview of the spatial and symmetry properties of binary spherical nanoparticle superlattices. $F_{\max}$ is the maximum possible fill fraction for each structure, achieved by choosing the nanoparticle radius ratio r_2/r_1 . $r_{1(F=0.6)}$ is the radius of the larger nanoparticle (NP1) for the chosen fill fraction $F = 0.6$. The group theory notations are from [29,30]. Under type, “sc” indicates simple cubic.

Structure		Parameters			Space group		Wyckoff	
Name	Type	$F_{\max}$	r_2/r_1	$r_{1(F=0.6)}$ (nm)	Symbol	Number	NP1	NP2
CsCl	sc	0.729	0.732	25	$Pm\bar{3}m$	221	1a	1b
NaCl	fcc	0.791	0.414	23	$Fm\bar{3}m$	225	4a	4b
ZnS	fcc	0.749	0.255	24	$F\bar{4}3m$	216	4a	4c
Cu ₃ Au	sc	0.636	0.414	28	$Pm\bar{3}m$	221	1a	3c

new structures into the analysis allows us to develop a set of symmetry selection rules for plasmon-polariton excitations in binary metallic supercrystals based on inversion symmetry that are not specific to a particular lattice structure.

This paper is organized as follows. First, we introduce our description of the supercrystal system and its excitations, as well as the methods used for the analysis and generalized findings, in Sec. II. In Sec. III we discuss supercrystals with the NaCl, ZnS, and Cu₃Au structures, complete with group theory tables and dispersion figures.

II. METHODS

We consider the optical excitations in cubic binary plasmonic superlattices, i.e., supercrystals with two plasmonic nanoparticles with different diameters arranged in a variety of cubic structures. In all of the investigated structures, the larger nanoparticle (NP1) is situated at the corner of the cubic unit cell, while the placement of a smaller nanoparticle (NP2) at different positions results in distinct symmetries, plasmon-polariton dispersions, and optical properties. The nanoparticles themselves are defined by their material, plasmon frequency, and radii r_1 (NP1) and r_2 (NP2).

We calculate the plasmon-polariton band structure with the formalism introduced in Ref. [16] (see the Appendix). In this approach, the total Hamiltonian is separated into its constituent parts. The first part describes the matter Hamiltonian for the bare dipolar and quadrupolar excitations of the nanoparticles. In this treatment we calculate them for a Drude metal within the quasistatic approximation [24,25]. The second part gives the evolution of the free photons, and the third part represents light-matter interaction. To account for the large sizes of the nanoparticles in the light-matter interaction, we expand the photon plane waves in spherical harmonics centered at each particle site, starting from a vector potential of a plane wave and its interactions with excitations of the electric charge distribution [16]. This approach enables the calculation of the band structure across the entire Brillouin zone of the supercrystal. It also allows us to determine the contribution of each excitation to each band, which plays an integral role in our symmetry analysis.

In order to focus on properties specific to the structure symmetry, we have to match material parameters across structures. The lattice constant a of the unit cell establishes the energy scale of the photons compared to the plasmon energies in the system. For the sake of comparison we select $a = 60$ nm as in Ref. [17]. The frequency of the dipole excitations of NP1

was set to $\omega_D^{(1)} = c\pi/2a$, so the wave vector for a photon energy $\hbar\omega_{pt,\mathbf{k}} = \hbar\omega_D$ falls in the middle of the first supercrystal Brillouin zone. The energy of the dipole and quadrupole plasmon excitations (ω_D and ω_Q) and the maximum coupling for each excitation in the nanoparticles are determined by the material composition of the nanoparticles and the surrounding medium. To simulate particles placed in vacuum, the dielectric constant of the surrounding medium and the dielectric constant that accounts for the screening by bound charges [26] are $\epsilon_\infty = \epsilon_m = 1$, so that plasmon frequencies of dipolar and quadrupolar excitations are $\omega_Q^{(1,2)} = 1.09\omega_D^{(1,2)}$ for both particles [Eqs. (A3) and (A4)]. The two nanoparticles in the unit cell of a binary supercrystal may differ in their plasmon frequencies [27,28], e.g., due to different material composition and size. We chose $\omega_D^{(2)} = 1.3\omega_D^{(1)}$, a value sufficiently large to prevent accidental degeneracies but sufficiently small to allow mixing of dipole and quadrupole bands.

The size of the particles compared to the lattice parameter determines the relative fill fractions for each nanoparticle, which govern the coupling parameters between dipoles, quadrupoles, and photons. We previously showed that for both monodisperse and binary supercrystals this parameter strongly affects the dispersion of the plasmonic bands and the strength of the light-matter interaction [16,17]. In order to simulate crystals with deep strong light-matter coupling, we choose the ratio between particle radii r_2/r_1 that allows for the maximum fill fraction $F_{\max}$ for each structure (see Table I). However, for the sake of comparison, we chose to scale all particles so that all the structures studied have the same fill, $F = 0.6$. The resulting sizes of the larger particle NP1 are also listed in Table I, while the ratio is kept constant. We choose this ratio because it also keeps the structures well-defined for our symmetry analysis, and with this choice of parameters, we can calculate the Rabi frequency Ω_R and the bare plasmon frequency ω_{pl}^t and compare the normalized coupling strength $\eta = \Omega_R/\omega_{pl}^t$ across different structures to assess the light-matter interaction. Ω_R can be found from the minimum energy splitting between the lower and upper plasmon polariton bands (divided by 2), and ω_{pl}^t can be found from a calculation of the bare plasmon dispersion [11,12,15]. The normalized coupling strength can be used to determine whether a given excitation of the system is in the ultrastrong ($0.1 < \eta < 1$) or deep strong ($\eta > 1$) coupling regime [11,12].

The final tool in our analytical tool kit is group theory analysis based on space group theory [31,32]. First, we determine the space group of each structure and the specific nonequivalent Wyckoff positions for each nanoparticle. They

are listed in Table I. A nanoparticle at a specific Wyckoff position has symmetry that is the same as or lower than that of the crystal itself. By using a character table for its group we can determine the symmetries of specific excitations. Dipole excitations transform like the linear displacement (x, y, z) , while quadrupole excitations behave like traceless quadratic displacements $(x^2 - y^2, 2z^2 - x^2 - y^2, xy, xz, yz)$. Finally, by examining the band representations of each of these excitations across the Brillouin zone of the structure, we can determine their irreducible representations (irreps) at each high-symmetry point and line of the first Brillouin zone. Selection rules for dipole and quadrupole plasmonic excitations are obtained by identifying modes that transform as the same irrep. These rules govern the existence, mixing, and degeneracy of bands irrespective of the material properties of the nanoparticles.

The symmetry analysis of the collective plasmonic and plasmon-polariton bands is similar to the well-known physics of electronic band formation through the coupling of atomic orbitals in crystal structures of semiconductors. By classifying electronic states into their respective irreducible representations, one can determine degeneracies, predict how bands will split under perturbations, and identify which optical transitions are permitted by symmetry [33]. p orbitals transform as dipoles, while d atomic orbitals correspond to quadrupoles. The main difference in our description of plasmonic supercrystals is the inclusion of photons and their interaction with dipole and quadrupole modes.

When light-matter interaction comes into the picture, the situation becomes more complicated. In the nanoparticle supercrystals the translational periodicity is on the same order as the wavelength of the involved photons. In this case, the dipole approximation fails, and the symmetry-based constraints to light-matter interaction must be considered explicitly [17]. We expand the photon field around each particle site, so that the photon transforms as the irreps of the transverse vectors in the group of the wave vector $\mathbf{k}$ for the particular Wyckoff position. With this, the photons couple to transverse dipolar excitations of each nanoparticle.

Our analysis of multiple structures shows that the inversion symmetry plays a crucial role in determining the mixing between the excitations of the different particles composing the structure. This behavior seems to be general for binary cubic superstructures and can be used as a rule-of-thumb to ascertain coupling between the excitations themselves. For high-symmetry points that preserve the inversion symmetry and where inversion does not exchange the nanoparticles, all energy bands induced by a given dipole or quadrupole state of an NP have the same parity under inversion. Moreover, the dipole of NP1 (D1) always has negative parity since a dipole located at the origin is inherently antisymmetric under inversion. The quadrupole has the parity opposite to that of the dipole. At high-symmetry points where the dipole of NP2 (D2) also exhibits negative parity under inversion, dipoles couple only to dipoles, while quadrupoles couple only to quadrupoles, with no mixing between the two (Fig. 1, left). In contrast, at points where the dipole of NP2 has positive parity, it will interact only with quadrupoles of NP1 (Q1) and vice versa, with no dipole-dipole and quadrupole-quadrupole mixing (Fig. 1, right). Photons transform as dipoles and always

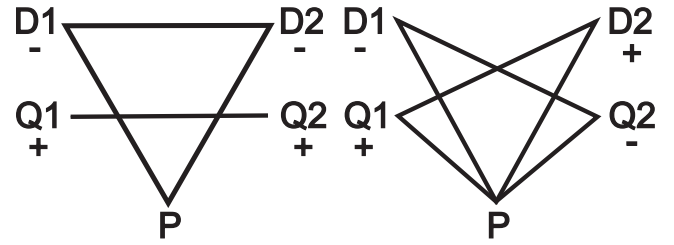


FIG. 1. Two options for coupling between nanoparticle excitations and light in binary plasmonic supercrystals with inversion symmetry. The solid lines represent coupling between dipoles (D1 and D2), quadrupoles (Q1 and Q2), and photons (P) in the supercrystal. + and - represent the positive and negative inversion symmetry of each excitation.

couple to some dipole-induced states. They will only couple to quadrupoles that have the same symmetry. Although the parity of each dipole depends on the choice of the coordinate system, the result is general: For supercrystals with exactly two different particles in a unit cell, there are only two possible coupling options (Fig. 1), which are determined by the symmetry of the group of the wave vector. The situation becomes more complicated as we add more nonequivalent particles, as we demonstrate with the example of an auricupride structure in Sec. III C. In the crystallographic directions that do not preserve inversion symmetry, mixing between all excitations is allowed by symmetry (see Sec. III B).

III. BINARY LATTICE STRUCTURES

To illustrate the wide variety of the symmetry-related light-matter properties of binary supercrystals, we discuss in this section the polaritonic dispersion of three select binary structures based on the microscopic dipole-quadrupole model and their symmetries. We assemble group theory tables that list the excitation symmetries at principal crystallographic directions. The coupling of the dipole- and quadrupole-induced plasmonic states with each other and to light can be read off these tables by identifying the dipole and quadrupole modes that transform as the same irreps. The irreps of plasmonic states that are identical to the photon irreps are shown in bold. These excitations couple to light. The number of energy bands and their degeneracy are determined by symmetry and can be found by counting the total number of irreps for each excitation.

A. Sodium chloride structure

Sodium chloride is one of the best-known binary structures. It can be conceptualized as the superposition of two fcc lattices with the corner of one lattice positioned at the center of the unit cell of the other. More formally, NaCl has an fcc Bravais lattice with a basis of two atoms, an Na atom at the origin and a Cl atom at the corner of the cubic unit cell. The NaCl structure group $\mathcal{G}_S$ is the symmorphic space group $Fm-3m$ (225) or O_h^5 [31,32]. Each nanoparticle occupies one of two inequivalent Wyckoff positions, $4a$ (NP1) and $4b$ (NP2) [29]. The dipoles of both nanoparticles transform as T_{1u} , and the quadrupoles transform as E_g and T_{2g} within

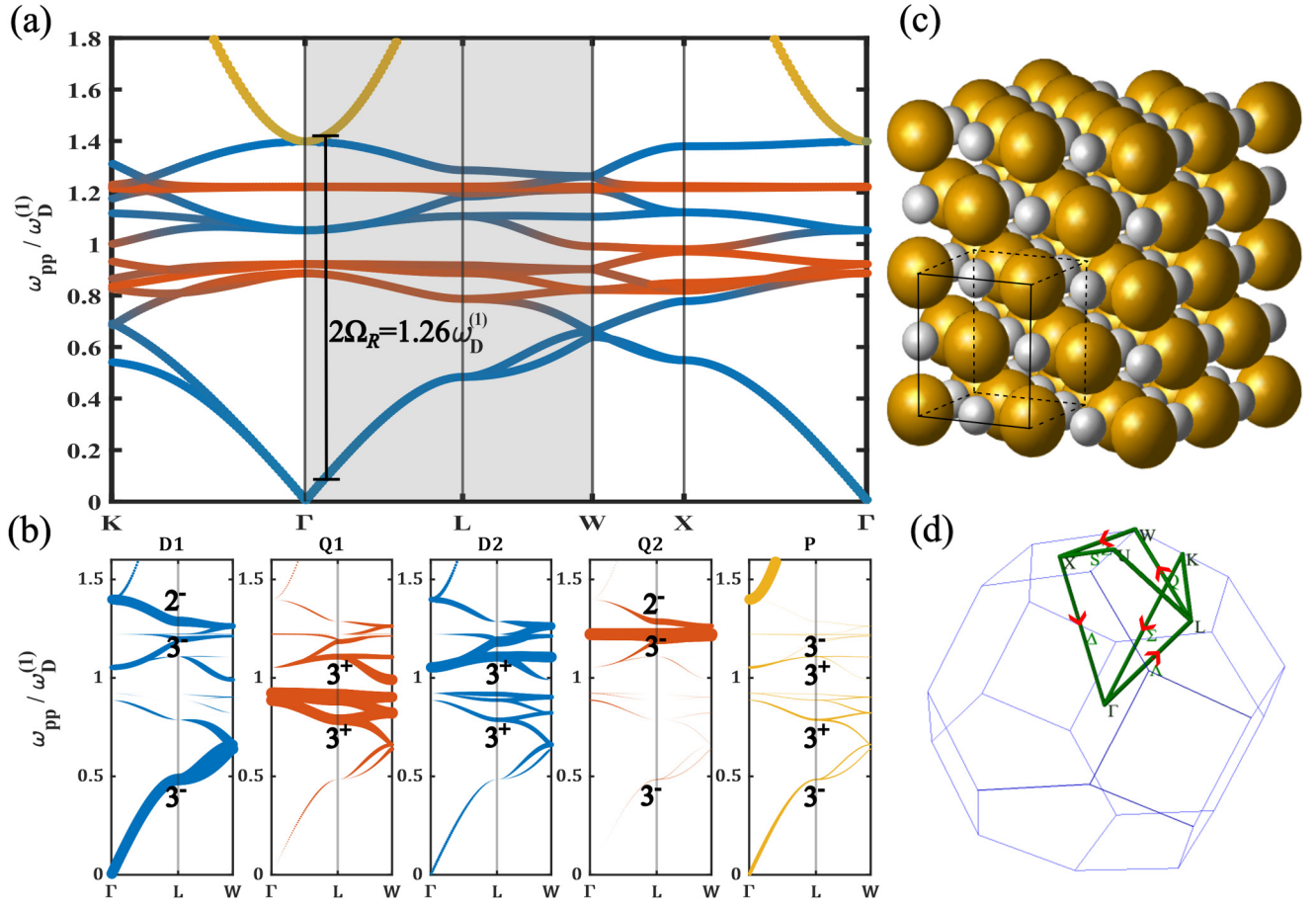


FIG. 2. (a) Plasmon-polariton dispersion of a NaCl-like supercrystal. Bands are colored according to their origin: dipoles are blue, quadrupoles are red, and photons are yellow. Bands of mixed origin are colored correspondingly. The energy scale is normalized to the dipole excitation of NP1. (b) The shaded area in (a) is decomposed into contributions from each excitation: D1 and D2 are the dipoles of the two nanoparticles in the unit cell, Q1 and Q2 are quadrupoles, and P are photons. Some of the bands at L are marked with their irreducible representations in order to illustrate how parity under inversion can provide insights into the coupling of excitations. (c) Nanoparticle supercrystal with the sodium chloride structure in real space. (d) First Brillouin zone of the fcc lattice in reciprocal space. Red arrows represent the path through the Brillouin zone in (a).

the O_h point group. The Brillouin zone has the shape of a truncated octahedron (mecon) and has four inequivalent high-symmetry points, Γ , X , L , and W [see Fig. 2(d)]. In Table II we show the irreducible representations induced by the dipole and quadrupole excitations for the particles in the Wyckoff positions of NP1 and NP2 in the NaCl-like structure for selected points and lines of the first Brillouin zone. The column titled “Photons” lists the irreps of the transverse dipole bands that couple to the photons of the first Brillouin zone. These representations are shown in bold in the principal directions with inversion symmetry present in order to illustrate which excitations exhibit the strongest light-matter coupling.

From Table II, we see that the dipole excitations of NP1 share irreducible representations with those of the photons in the first Brillouin zone in all high-symmetry directions. On the other hand, quadrupole excitations are more restricted and, for instance, share no irreducible representation with photons or dipoles at the Γ and X points, indicating that quadrupoles at these points are decoupled from both photons and dipoles. At specific directions, some of the quadrupole, dipole, and photon excitations have common irreducible representations

and may couple, possibly leading to the formation of hybrid dipole-quadrupole-photon modes.

To better illustrate these observations, we show in Fig. 2(a) the dispersion of the supercrystal with the NaCl structure. We plot the energy of each excitation at different high-symmetry points and lines of the first Brillouin zone of the structure [red arrows in Fig. 2(d) illustrate our path]. In accordance with the structure symmetry, the energy bands can degenerate or split at different parts of the Brillouin zone. The bands are color coded according to the contributing excitations. Dipoles are blue, quadrupoles are red, and photons are yellow. Since some excitations couple to each other, bands of mixed origin are shaded accordingly. From the dispersion, we extract the value of the Rabi frequency Ω_R , shown in Fig. 2(a), and calculate the bare plasmon energy (without including photons). Ω_R was obtained at the point of intersection of the bare photon and plasmon bands, where the energy separation between the lower and upper plasmon polariton bands is minimal. The normalized coupling strength $\eta = \Omega_R / \omega_{pl}' = 1.13$ in the deep-strong coupling regime, which is characteristic of plasmonic supercrystals [11,12].

TABLE II. Plasmon-polariton symmetry in the NaCl-like structure. The irreducible representations (irreps) of the photon and the dipole- and quadrupole-induced states in a NaCl binary supercrystal are listed. The dipoles and quadrupoles were placed at the Wyckoff positions of the plasmonic nanoparticles, NP1 (4a) and NP2 (4b). The high-symmetry points and lines are indicated by their symbol and $\mathbf{k}$ vectors [see Fig. 2(d)]. The photon transforms as the irreps of the transverse vectors. Modes that transform as the same irreps couple to each other. The irreps of all excitations coupling to light are shown in bold.

Symmetry point		Photon		Dipole		Quadrupole	
Symbol	$\mathbf{k}$ vector	(4a)	(4b)	NP1 (4a)	NP2 (4b)	NP1 (4a)	NP2 (4b)
Γ	(0,0,0)	Γ_4^-	Γ_4^-	Γ_4^-	Γ_4^-	$\Gamma_3^+ \oplus \Gamma_5^+$	$\Gamma_3^+ \oplus \Gamma_5^+$
X	(0,1,0)	$\mathbf{X}_5^-$	$\mathbf{X}_5^-$	$X_3^- \oplus X_5^-$	$X_3^- \oplus X_5^-$	$X_1^+ \oplus X_2^+ \oplus X_4^+ \oplus X_5^+$	$X_1^+ \oplus X_2^+ \oplus X_4^+ \oplus X_5^+$
L	(1/2, 1/2, 1/2)	$\mathbf{L}_3^-$	$\mathbf{L}_3^+$	$L_2^- \oplus L_3^-$	$L_1^+ \oplus L_3^+$	$L_1^+ \oplus 2L_3^+$	$L_2^- \oplus 2L_3^-$
W	(1/2, 1, 0)	W_5	W_5	$W_1 \oplus W_5$	$W_2 \oplus W_5$	$W_1 \oplus W_2 \oplus W_3 \oplus W_5$	$W_1 \oplus W_2 \oplus W_4 \oplus W_5$
$\Delta = \overline{\Gamma X}$	(0, v , 0)	Δ_5	Δ_5	$\Delta_1 \oplus \Delta_5$	$\Delta_1 \oplus \Delta_5$	$\Delta_1 \oplus \Delta_2 \oplus \Delta_3 \oplus \Delta_5$	$\Delta_1 \oplus \Delta_2 \oplus \Delta_3 \oplus \Delta_5$
$\Lambda = \overline{\Gamma L}$	(u , u , u)	Λ_3	Λ_3	$\Lambda_1 \oplus \Lambda_3$	$\Lambda_1 \oplus \Lambda_3$	$\Lambda_1 \oplus 2\Lambda_3$	$\Lambda_1 \oplus 2\Lambda_3$
$\Sigma = \overline{\Gamma X}$	(u , u , 0)	$\Sigma_2 \oplus \Sigma_3$	$\Sigma_2 \oplus \Sigma_3$	$\Sigma_1 \oplus \Sigma_2 \oplus \Sigma_3$	$\Sigma_1 \oplus \Sigma_2 \oplus \Sigma_3$	$2\Sigma_1 \oplus \Sigma_2 \oplus \Sigma_3 \oplus \Sigma_4$	$2\Sigma_1 \oplus \Sigma_2 \oplus \Sigma_3 \oplus \Sigma_4$
$V = \overline{WX}$	(u , 1, 0)	$V_3 \oplus V_4$	$V_3 \oplus V_4$	$V_1 \oplus V_3 \oplus V_4$	$V_1 \oplus V_3 \oplus V_4$	$2V_1 \oplus V_2 \oplus V_3 \oplus V_4$	$2V_1 \oplus V_2 \oplus V_3 \oplus V_4$
$Q = \overline{LW}$	(1/2, v , $1-v$)	$Q_1 \oplus Q_2$	$Q_1 \oplus Q_2$	$Q_1 \oplus 2Q_2$	$2Q_1 \oplus Q_2$	$3Q_1 \oplus 2Q_2$	$2Q_1 \oplus 3Q_2$

The selection rules for the dipole-quadrupole coupling discussed in Sec. II can be seen by examining Fig. 2(b), where we show the shaded area of the Brillouin zone in Fig. 2(a), decomposed into contributions from the dipoles and quadrupoles of each nanoparticle as well as photons. At the Γ point, all quadrupole irreducible representations are of even parity (+), while all dipole irreducible representations are odd upon inversion. Dipoles and quadrupoles are completely decoupled at this high-symmetry point, and photons follow suit, coupling only to dipoles. On the other hand, according to group theory, the L_2^- quadrupole of NP2 can couple to the longitudinal dipole excitation of NP1 at L since they have the same irreducible representation. This coupling is seen in the top band at L , to which the other dipole and quadrupole make no contribution at this particular high-symmetry point, as all their symmetries have the opposite parity (+). The situation is similar in all bands at L : The dipole of NP1 and the quadrupole of NP2 have the same irreps and couple to each other, as do their counterparts. The photons exhibit a notable degree of coupling to excitations stemming from all dipoles and quadrupoles, including those for which direct coupling is not permitted. The transverse band of D1 exhibits L_3^- symmetry, whereas D2 displays L_3^+ symmetry with opposite parity under inversion. The coupling between these dipoles is forbidden, as evidenced by their dispersion [Fig. 2(b)]. Nevertheless, the photons couple to both of these bands with comparable contributions. This phenomenon can be attributed to the methodology employed in our calculations, in which photons are considered to be situated at both particle sites. Quadrupoles are also included in the calculation and introduce additional bands with the same L_3^- and L_3^+ symmetries, which permit the coupling to the corresponding dipoles, resulting in these bands also coupling to the photons with comparable contributions at L [see Fig. 2(b)].

Notably, the same symmetry selection rules apply to semiconductors with NaCl structure, such as lead salts (e.g., PbSe, PbTe), providing a neat comparison for their quasiparticle states. The electronic structure [34] and optical properties [35] of lead salts are well-known, and the inversion symmetry

serves as a coupling marker as well. In PbTe [36] the direct band gap occurs at the same L high-symmetry point, where the valence and conduction bands have opposite inversion symmetries. Like in the supercrystal with the same structure, at Γ these bands have the same negative inversion symmetry and the same irreps, for example, the twofold L_3^+ band and single-fold L_1^+ degenerate into a threefold Γ_4^- band, the same as L_3^- and L_2^- . Therefore, bands of the electronic structure of semiconductors have the same degeneracies and symmetries, which can be taken from Table II. Near the valence band maximum, states often derive primarily from anion p orbitals, whose dipolar character and symmetry dictate the heavy-hole, light-hole, and split-off bands [37]. The composition of the conduction band is less clear-cut; however, research has demonstrated that d orbitals (which have quadrupolar character) can mix into conduction-band states and thus affect the details of the band structure [38].

Finally, at the W point, the inversion symmetry is not conserved, leading to a limited number of irreps that repeat across excitations. As a result, almost every band at W contains contributions from all sources, forming dipole-quadrupole-photon modes. This kind of behavior is seen throughout the Brillouin zone, where dipoles, quadrupoles, and photons belonging to the same representation can couple to form hybrid states. Here, as discussed in Sec. II, parity upon inversion appears to be a key marker of dipole-quadrupole interactions.

B. Zinc blende structure

Zinc blende is another well-known binary cubic structure that, at first glance, appears strikingly similar to the sodium chloride structure discussed in the previous section. Both structures can be conceptualized as the superposition of two fcc lattices, but in the case of zinc blende NP2 is even smaller and is located at the (1/4, 1/4, 1/4) site, rather than at the center of the conventional unit cell.

The group $\mathcal{G}_S$ of the ZnS structure is the symmorphic space group $F-43m$ (216) or T_d^2 [31,32]. Each nanoparticle occupies

TABLE III. Plasmon-polariton symmetry in the ZnS structure. The high-symmetry points and lines are indicated by their symbol and $\mathbf{k}$ vectors [see Fig. 3(d)]. Without inversion symmetry, every excitation couples to light.

Symmetry point		Photon (4a,4c)	Dipole		Quadrupole	
Symbol	$\mathbf{k}$ vector		NP1 (4a)	NP2 (4c)	NP1 (4a)	NP2 (4c)
Γ	(0,0,0)	Γ_4	Γ_4	Γ_4	$\Gamma_3 \oplus \Gamma_4$	$\Gamma_3 \oplus \Gamma_4$
X	(0,1,0)	X_5	$X_3 \oplus X_5$	$X_3 \oplus X_5$	$X_1 \oplus X_2 \oplus X_3 \oplus X_5$	$X_1 \oplus X_3 \oplus X_4 \oplus X_5$
L	(1/2, 1/2, 1/2)	L_3	$L_1 \oplus L_3$	$L_1 \oplus L_3$	$L_1 \oplus 2L_3$	$L_1 \oplus 2L_3$
W	(1/2, 1, 0)	$W_2 \oplus W_3$	$W_2 \oplus W_3 \oplus W_4$	$W_1 \oplus W_2 \oplus W_3$	$W_1 \oplus 2W_2 \oplus W_3 \oplus W_4$	$W_1 \oplus W_2 \oplus 2W_3 \oplus W_4$
$\Delta = \overline{\Gamma X}$	(0, v , 0)	$\Delta_3 \oplus \Delta_4$	$\Delta_1 \oplus \Delta_3 \oplus \Delta_4$	$\Delta_1 \oplus \Delta_3 \oplus \Delta_4$	$2\Delta_1 \oplus \Delta_2 \oplus \Delta_3 \oplus \Delta_4$	$2\Delta_1 \oplus \Delta_2 \oplus \Delta_3 \oplus \Delta_4$
$\Lambda = \overline{\Gamma L}$	(u , u , u)	Λ_3	$\Lambda_1 \oplus \Lambda_3$	$\Lambda_1 \oplus \Lambda_3$	$\Lambda_1 \oplus 2\Lambda_3$	$\Lambda_1 \oplus 2\Lambda_3$
$\Sigma = \overline{\Gamma X}$	(u , u , 0)	$\Sigma_1 \oplus \Sigma_2$	$2\Sigma_1 \oplus \Sigma_2$	$2\Sigma_1 \oplus \Sigma_2$	$3\Sigma_1 \oplus 2\Sigma_2$	$3\Sigma_1 \oplus 2\Sigma_2$
$V = \overline{WX}$	(u , 1, 0)	$V_1 \oplus V_2$	$V_1 \oplus 2V_2$	$2V_1 \oplus V_2$	$3V_1 \oplus 2V_2$	$2V_1 \oplus 3V_2$
$Q = \overline{LW}$	(1/2, v , 1 - v)	$2Q_1$	$3Q_1$	$3Q_1$	$5Q_1$	$5Q_1$

one of two inequivalent Wyckoff positions, 4a (NP1) and 4c (NP2) [29]. As the ZnS structure lacks inversion symmetry, the three quadrupoles with bases xy , yz , and xz will always have the same irreducible representations of the dipoles, see Table III. This leads to dipole-quadrupole interaction in the entire Brillouin zone. For instance, at Γ the dipoles of both nanoparticles transform as T_2 ; three of the quadrupoles also have T_2 symmetry, while the other two transforms as the E irreducible representation. As photons in the first Brillouin zone transform in a way similar to the dipoles, quadrupoles should also be able to couple to photons efficiently.

Figure 3(a) depicts the dispersion of the supercrystal with a zinc blende structure. Given that ZnS is also an fcc structure, it has the same Brillouin zone (BZ) as NaCl, which facilitates comparison. However, since the ratio between the particle sizes is smaller (the ratio resulting in the maximum metal fill fraction is $r_2/r_1 = 0.255$ for ZnS, compared to 0.414 for NaCl), the dipole and quadrupole bands related to NP2 are much less dispersive even for the large fill fractions used in this calculation, sufficient to reach a deep-strong light-matter coupling regime. This is mainly an effect of the reduced size of the particle compared to the size of the unit cell, which weakens its dipole and quadrupole moment and interactions with other particles, even though the total metal fill fraction is kept the same at $F = 0.6$. Although there are no forbidden couplings between excitations, symmetry still determines which bands will be degenerate in which high-symmetry directions. For example, the lower plasmon-polariton band has twofold L_3 symmetry, then splits when we move toward the W point of the BZ, where it has one-dimensional W_2 and W_3 symmetries. At X it is degenerate again, belonging to the twofold X_5 representation.

The calculated normalized coupling strength $\eta = 1.08$ is slightly lower than in NaCl. This can also be attributed to the weaker interactions of the smaller particle. In Fig. 3(b) we decompose our dispersion calculation into contributions from different excitations. Although dipoles and quadrupoles are allowed to couple throughout the Brillouin zone, this interaction is effective only in the regions where the two types of excitations have similar energies, which in this case happens near the W high-symmetry point.

C. Auricupride structure

Auricupride is another cubic structure with unique properties. Its unit cell has one large particle in the corner (NP1), while the smaller particles (NP2–NP4) occupy the faces of the cube, a Wyckoff position with threefold multiplicity; i.e., three identical nanoparticles occupy nonequivalent sites which exchange through the point group operations of the structure. For some high-symmetry directions, the parity upon inversion of these smaller nanoparticles is opposite to that of NP1, providing an excellent test bed for understanding the role of the inversion symmetry on the selection rules for dipole-quadrupole-photon coupling.

Cu_3Au has a simple cubic structure and space group $Pm-3m$ (221) or O_h^1 [31,32]. NP1 at (0, 0, 0) occupies Wyckoff position 1a, while the smaller nanoparticles occupy Wyckoff position 3c, with crystallographic sites (0, 1/2, 1/2), (1/2, 1/2, 0), and (1/2, 0, 1/2). To fully describe this structure, we need to consider the excitations of each nanoparticle separately, which doubles the number of dipolar and quadrupolar bands in our calculation compared to all other structures we considered. In terms of symmetry analysis, this brings a new perspective for supercrystals because the 3c Wyckoff position has a lower symmetry than the crystal structure itself, making them part of the $4/mmm$ or $D4_h$ group, which is a subgroup of the symmetric space group $Pm-3m$ of the auricupride structure. The dipole of NP1 transforms as T_{1u} , and the quadrupole transforms as E_g and T_{2g} , just like the excitations of NP1 and NP2 in CsCl and NaCl. But for NP2–NP4 of Cu_3Au the situation is different: Their dipoles transform as E_u and A_{2u} , and quadrupoles transform as B_{1g} , B_{2g} , E_g , and A_{1g} , increasing the number of irreps just like we increased the number of bands in our calculation.

The increased number of particles leads to a large number of intermediate bands [see Fig. 4(a)]. The lower plasmon-polariton band has lower energy than in other structures, and so do the bare plasmon excitations. As a result, although the Rabi frequency Ω_R is similar across all structures, the Cu_3Au supercrystal has a significantly higher normalized coupling strength, $\eta = 1.35$, while the metal fill fraction remains the same. For monodisperse supercrystals, there is a direct correlation between coupling strength and fill fraction [1,16], but as

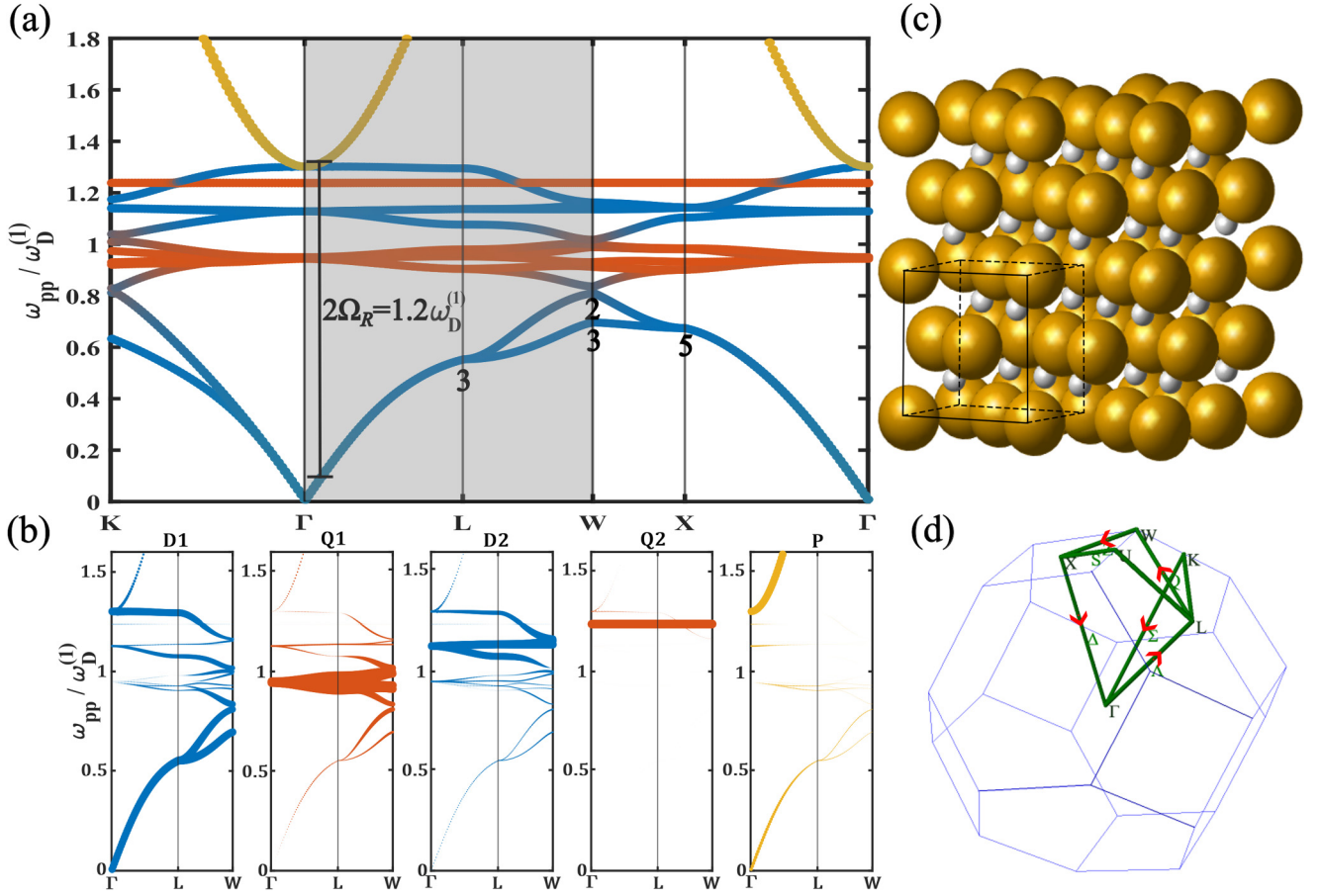


FIG. 3. (a) Plasmon-polariton dispersion of a ZnS-like supercrystal. (b) The shaded area in (a) is decomposed into contributions from each excitation. (c) Nanoparticle supercrystal with zinc blende structure in real space. (d) First Brillouin zone of the fcc lattice in reciprocal space. Red arrows represent the path through the BZ in (a).

the number of particles increases, the relation becomes more complex. A more detailed analysis of this effect across supercrystal structures with different numbers of nonequivalent particles will be the focus of a future study.

Inversion symmetry serves as a proxy to evaluate whether dipoles, quadrupoles, and photons couple. For instance, at the Γ and R high-symmetry points, all dipoles and photons

have negative parity upon inversion, while all quadrupole modes have positive parity. Quadrupoles are thus decoupled from both dipoles and first Brillouin zone photons at these points. On the other hand, at the M and X points, dipoles and quadrupoles of different particles can have positive or negative parity, allowing for dipole-quadrupole mixing and dipole-quadrupole-photon mixing.

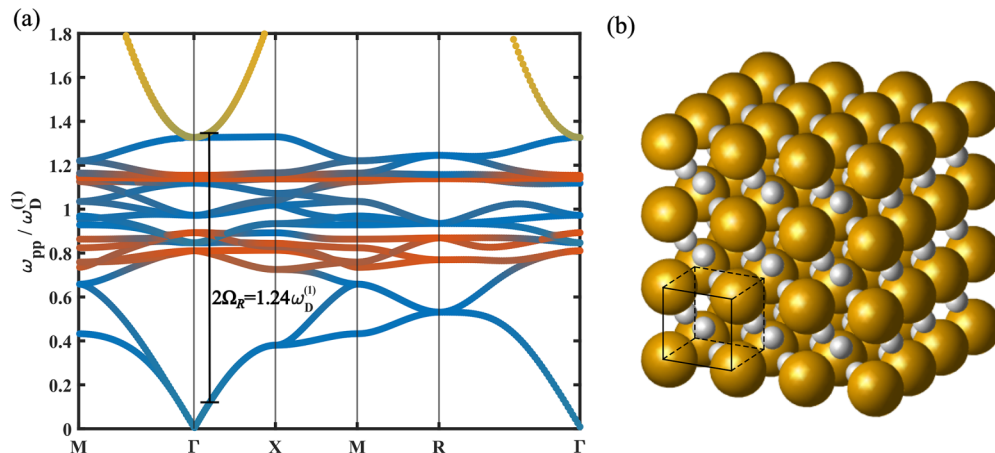


FIG. 4. (a) Plasmon-polariton dispersion of a Cu₃Au-like supercrystal. The threefold multiplicity of Wyckoff position $3c$ of smaller nanoparticles leads to an increased number of bands. (b) Nanoparticle supercrystal with auricupride structure in real space.

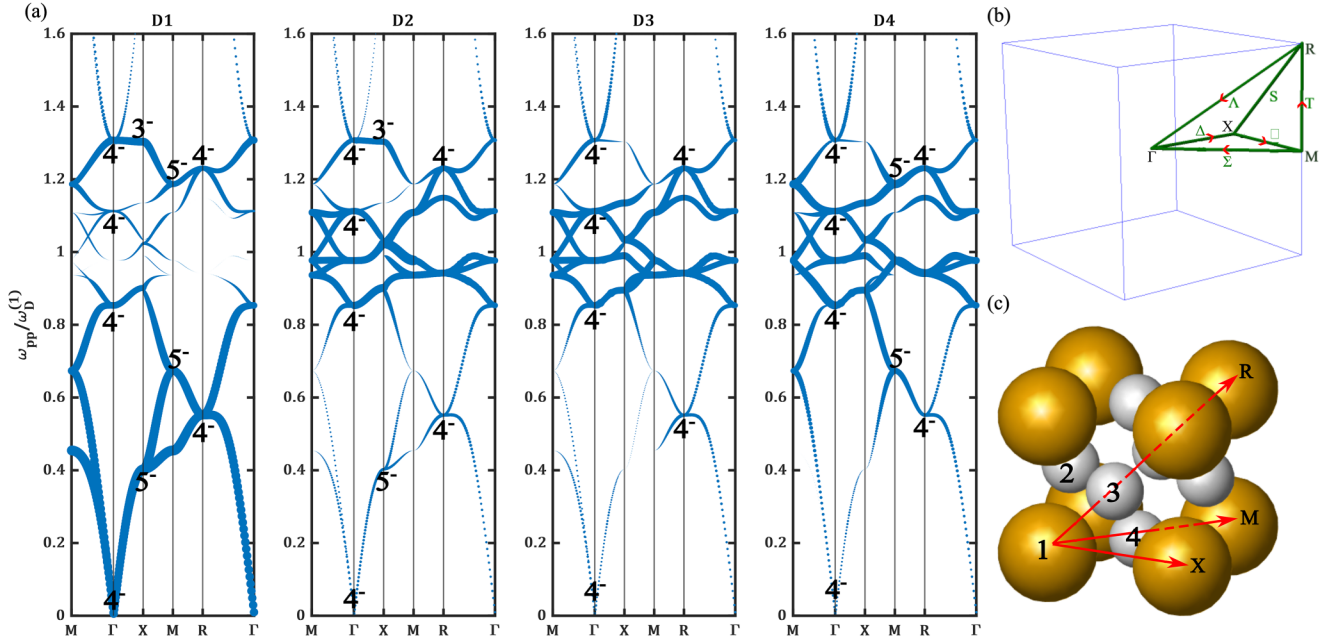


FIG. 5. (a) Decomposition of plasmon-polariton dispersion of a binary plasmonic supercrystal with a structure inspired by Cu_3Au into contributions from the dipoles of NP1–NP4. Some bands are marked with their irreducible representations to illustrate the coupling between different excitations. Only the bands that couple to the dipole of the larger particle (NP1) are marked. (b) Simple cubic Brillouin zone with its high-symmetry points and lines. Black arrows represent primitive reciprocal lattice vectors. Green arrows represent primitive lattice vectors. (c) Real-space unit cell of the auricupride structure.

In Fig. 5 we show the decomposition of our dispersion calculation into the contributions of all four dipoles. For simplicity, we do not include the quadrupoles in the calculation, as there are already 12 dipolar bands. The Brillouin zone is simple cubic with four inequivalent high-symmetry points, Γ , X , R , and M [see Fig. 5(b)]. We first consider the Γ and R points that are located in the center and corner of the Brillouin zone, respectively [Fig. 5(b)]. Excitations at R correspond to waves traveling along the (111) crystallographic direction in real space [the arrow labeled R in Fig. 5(c)]. NP2–NP4 are equivalent for this direction, as the threefold rotation axis exchanges them. This is reflected in Table IV and in Fig. 5(a). Dipolar bands of all four NPs degenerate at this point, in agreement with group theory. Also, dipoles in the different particles all couple with each other, as they have the same irreps [see Fig. 5(a)]. Quadrupoles have the inversion opposite to that of the dipoles, so there is no dipole-quadrupole interaction at the R high-symmetry point (not shown).

The behavior of excitations at the X and M high-symmetry points differs from that at the R point. When describing these excitations in real space, we see that for the X and M directions the three smaller nanoparticles are no longer equivalent. In the case of X , waves travel in the (100) direction, so only NP3 and NP4 can be exchanged by rotation around the axis, while NP2 stands apart [see Fig. 5(c)]. As a result, NP3 and NP4 have parity opposite to that of NP1 and NP2. On the other hand, for the M direction selected in Fig. 5(c), NP4 finds itself on the real-space vector defining the propagation direction, different from NP2 and NP3. Comparing our group theory table to the dispersion decomposition, we can match the bands with irreps by noting which dipoles couple to each

other. In Fig. 5(a) we label some of the bands with their irreps to illustrate this process. The odd parity dipoles (NP2 for X and NP4 for M) also couple to the odd dipoles in NP1, while the dipole states in the remaining two particles are even upon inversion and couple to each other. In Table IV we split these irreps into two rows for M and X to illustrate the fact that they do not couple with each other. When we add quadrupoles to the analysis, the situation is unchanged: The irreps with opposite inversion symmetries are forbidden from coupling. This makes Cu_3Au an excellent example of how inversion symmetry plays an important role in determining the matter-matter (and, to some extent, light-matter) interactions in plasmonic supercrystals.

IV. CONCLUSIONS

In summary, we analyzed the symmetry and light-matter coupling of plasmon-polaritons in selected cubic binary nanoparticle supercrystals, focusing on three prototypical crystal structures derived from sodium chloride, zinc blende, and auricupride. The microscopic model incorporates the dipole and quadrupole modes of the nanoparticle building blocks and their coupling to far-field photons, thereby including retardation effects explicitly in our treatment. To highlight the role of crystal structure and its symmetry on the properties of plasmon-polaritons, we used comparable materials parameters in the simulation of all superlattices. This led us to a set of selection rules for the mixing of dipole- and quadrupole-induced collective states and light that apply to all cubic supercrystals. We showed that inversion and site symmetry govern the existence, interaction, and degeneration of bands, independent of the material properties of

TABLE IV. Polariton symmetry in the Cu₃Au structure. The high-symmetry points and lines are indicated by their symbol and **k** vectors [see Fig. 5(b)]. The increased number of nonequivalent nanoparticles leads to a larger number of representations; therefore, for clarity, we use two rows for the irreps with positive and negative inversion for *M* and *X*.

Symmetry	Photon		Dipole		Quadrupole	
	(1a)	(3c)	NP1 (1a)	NP2–NP4 (3c)	NP1 (1a)	NP2–NP4 (3c)
Γ	Γ_4^-		Γ_4^-	$2\Gamma_4^- \oplus \Gamma_5^-$	$\Gamma_3^+ \oplus \Gamma_5^+$	$\Gamma_1^+ \oplus \Gamma_2^+ \oplus 2\Gamma_3^+ \oplus \Gamma_4^+ \oplus \Gamma_5^+$
<i>R</i>	$\mathbf{R}_4^-$	$\mathbf{R}_5^-$	$\mathbf{R}_4^-$	$R_2^- \oplus R_3^- \oplus R_4^- \oplus \mathbf{R}_5^-$	$R_3^+ \oplus R_5^+$	$R_1^+ \oplus R_3^+ \oplus 2R_4^+ \oplus 2R_5^+$
<i>M</i>	$\mathbf{M}_5^-$	$\mathbf{M}_5^+$	$M_3^- \oplus \mathbf{M}_5^-$	$M_2^- \oplus \mathbf{M}_5^- \oplus M_1^+ \oplus M_2^+ \oplus M_3^+ \oplus M_4^+ \oplus \mathbf{M}_5^+$	$M_1^+ \oplus M_2^+ \oplus M_4^+ \oplus \mathbf{M}_5^+$	$M_1^- \oplus M_2^- \oplus M_3^- \oplus M_4^- \oplus 3\mathbf{M}_5^- \oplus M_1^+ \oplus M_3^+ \oplus M_4^+ \oplus \mathbf{M}_5^+$
<i>X</i>	$\mathbf{X}_5^-$	$\mathbf{X}_5^+$	$X_3^- \oplus \mathbf{X}_5^-$	$X_3^- \oplus \mathbf{X}_5^- \oplus X_1^+ \oplus X_2^+ \oplus 2\mathbf{X}_5^+$	$X_1^+ \oplus X_2^+ \oplus X_4^+ \oplus \mathbf{X}_5^+$	$X_1^- \oplus X_2^- \oplus 2X_3^- \oplus 2X_4^- \oplus 2\mathbf{X}_5^- \oplus X_1^+ \oplus X_2^+ \oplus X_4^+ \oplus \mathbf{X}_5^+$
$\Delta = \overline{\Gamma X}$	Δ_5		$\Delta_1 \oplus \Delta_5$	$2\Delta_1 \oplus \Delta_2 \oplus 3\Delta_5$	$\Delta_1 \oplus \Delta_2 \oplus \Delta_3 \oplus \Delta_5$	$3\Delta_1 \oplus 3\Delta_2 \oplus 2\Delta_3 \oplus \Delta_4 \oplus 3\Delta_5$
$\Sigma = \overline{\Gamma M}$	$\Sigma_2 \oplus \Sigma_3$		$\Sigma_1 \oplus \Sigma_2 \oplus \Sigma_3$	$3\Sigma_1 \oplus 3\Sigma_2 \oplus 2\Sigma_3 \oplus \Sigma_4$	$2\Sigma_1 \oplus \Sigma_2 \oplus \Sigma_3 \oplus \Sigma_4$	$5\Sigma_1 \oplus 4\Sigma_2 \oplus 3\Sigma_3 \oplus 3\Sigma_4$
$\Lambda = \overline{\Gamma R}$	Λ_3		$\Lambda_1 \oplus \Lambda_3$	$2\Lambda_1 \oplus \Lambda_2 \oplus 3\Lambda_3$	$\Lambda_1 \oplus 2\Lambda_3$	$3\Lambda_1 \oplus 2\Lambda_2 \oplus 5\Lambda_3$
$T = \overline{MR}$	T_5		$T_1 \oplus T_5$	$T_1 \oplus T_2 \oplus 2T_3 \oplus T_4 \oplus 2T_5$	$T_1 \oplus T_2 \oplus T_3 \oplus T_5$	$2T_1 \oplus T_2 \oplus 2T_3 \oplus 2T_4 \oplus 4T_5$
$Z = \overline{MX}$	$Z_3 \oplus Z_4$		$Z_1 \oplus Z_3 \oplus Z_4$	$3Z_1 \oplus 2Z_2 \oplus Z_3 \oplus 3Z_4$	$2Z_1 \oplus Z_2 \oplus Z_3 \oplus Z_4$	$4Z_1 \oplus 3Z_2 \oplus 3Z_3 \oplus 5Z_4$
$S = \overline{RX}$	$S_2 \oplus S_3$		$S_1 \oplus S_2 \oplus S_3$	$2S_1 \oplus 2S_2 \oplus 3S_3 \oplus 2S_4$	$2S_1 \oplus S_2 \oplus S_3 \oplus S_4$	$4S_1 \oplus 3S_2 \oplus 4S_3 \oplus 4S_4$

the constituent nanoparticle building blocks. The strength of light-matter coupling in the different cubic crystals depends on the size and number of nonequivalent nanoparticles in the conventional unit cell. Our study provides a comprehensive analysis of each supercrystal with a full description of the lattice, its energy bands, a dispersion figure, and a group theory table. These results will be useful for manipulating and optimizing the optical response of binary plasmonic superlattices. Such materials are now available and will allow us to tailor light-matter coupling in the ultrastrong coupling regime. Our results will also prove useful in designing superlattices with a given property, such as polaritonic band gaps in their electromagnetic spectrum. Finally, the symmetry results presented by us apply to all artificial structures that are made from building blocks with optical dipole and quadrupole transitions, including quantum dot superlattices and molecular crystals.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [39].

APPENDIX: QUANTUM MICROSCOPIC PLASMON-POLARITON MODEL

Our model describes the optical excitations of a lattice of two types of plasmonic nanoparticles, arranged in a variety of

cubic structures. This approach involves formulating the total Hamiltonian as

$$\mathcal{H} = \mathcal{H}_M + \mathcal{H}_L + \mathcal{H}_{LM}. \quad (\text{A1})$$

$\mathcal{H}_M$ describes the matter Hamiltonian for the bare excitations of the nanoparticles, $\mathcal{H}_L$ gives the evolution of the free photons, and $\mathcal{H}_{LM}$ gives the light-matter interaction. The Hamiltonian for the matter part is

$$\begin{aligned} \mathcal{H}_M = & \sum_{\sigma} \hbar \omega_{\sigma} b_{\mathbf{k},\sigma} b_{\mathbf{k},\sigma}^{\dagger} \\ & + \sum_{\sigma,\sigma'} \hbar \sqrt{\Lambda_{\sigma} \Lambda_{\sigma'}} S_{\sigma\sigma'}^{\bar{\nu}\bar{\nu}'}(\mathbf{k}) (b_{\mathbf{k},\sigma} + b_{-\mathbf{k},\sigma}) \\ & \times (b_{\mathbf{k},\sigma'} + b_{-\mathbf{k},\sigma'}), \end{aligned} \quad (\text{A2})$$

where $\sigma = \{j, \nu\}$, with $j = 1, 2, \dots$, specifies the site in the unit cell and $\nu = x, y, z, x^2 - y^2, x^2 + y^2 - 2z^2, xy, yz, xz$ specify the dipole ($\bar{\nu} = D$) and quadrupole ($\bar{\nu} = Q$) bands. ω_{σ} is the bare energy for dipole and quadrupole excitations for each of the nanoparticles, and the factor $S_{\sigma\sigma'}^{\bar{\nu}\bar{\nu}'}(\mathbf{k})$ differs depending on whether $\bar{\sigma}$ is (j, D) for $\nu = x, y, z$ or (j, Q) for $\nu = x^2 + y^2 - 2z^2, xy, yz, xz$. $S_{\sigma\sigma'}^{DD}$, $S_{\sigma\sigma'}^{DQ}$, and $S_{\sigma\sigma'}^{QQ}$ describe, in reciprocal space, the interaction between dipoles and quadrupoles in the crystal lattice [40]. We posit, furthermore, that the plasmons' frequency in the metallic nanoparticles can be adequately described by the Drude model, $\epsilon = \epsilon_{\infty} - \omega_p^2/\omega^2$. In the quasistatic approximation, these plasmon frequencies are

$$\omega_D = \frac{\omega_p}{\sqrt{\epsilon_{\infty} + 2\epsilon_m}} \quad (\text{A3})$$

and

$$\omega_Q = \frac{\omega_p}{\sqrt{\epsilon_{\infty} + (3/2)\epsilon_m}}, \quad (\text{A4})$$

where ϵ_m is the dielectric constant of the surrounding material. The coupling parameters Λ_σ are given by

$$\Lambda_{j,D} = \frac{9\epsilon_m\omega_{j,D}}{8\pi(\epsilon_\infty + 2\epsilon_m)}F_j \quad (\text{A5})$$

and

$$\Lambda_{j,Q} = \left(\frac{3}{4\pi}\right)^{5/3} \frac{5\epsilon_m\omega_{j,Q}}{12(\epsilon_\infty + (3/2)\epsilon_m)}F_j^{5/3}, \quad (\text{A6})$$

where $F_j = V_j/V_{uc}$ is the ratio between the particular nanoparticle volume V_j and the volume of the supercrystal unit cell V_{uc} .

The free photon Hamiltonian is trivially described by $\mathcal{H}_L = \sum_{\mathbf{k},\lambda} \hbar\omega_{p,\mathbf{k}}c_{\mathbf{k},\lambda}^\dagger c_{\mathbf{k},\lambda}$, while the light-matter interaction is given by two parts, $\mathcal{H}_{LM} = \mathcal{H}_{LM}^{(1)} + \mathcal{H}_{LM}^{(2)}$, with

$$\mathcal{H}_{LM}^{(1)} = i\hbar \sum_{\mathbf{k},\mathbf{G},\lambda,\sigma} \omega_{\bar{\nu}} \xi_{\lambda,\mathbf{G}}^\sigma (b_{-\mathbf{k},\sigma}^\dagger - b_{\mathbf{k},\sigma}) (c_{-\mathbf{k}-\mathbf{G},\lambda} + c_{\mathbf{k}+\mathbf{G},\lambda}^\dagger) \quad (\text{A7})$$

and

$$\begin{aligned} \mathcal{H}_{LM}^{(2)} = \hbar \sum_{\mathbf{k},\lambda,\lambda',\mathbf{G},\mathbf{G}'} \Xi_{\mathbf{G},\mathbf{G}'}^{\lambda\lambda'}(\mathbf{k}) & (c_{-\mathbf{k}-\mathbf{G}',\lambda'}^\dagger + c_{\mathbf{k}+\mathbf{G}',\lambda'}) \\ & \times (c_{-\mathbf{k}-\mathbf{G},\lambda} + c_{\mathbf{k}+\mathbf{G},\lambda}^\dagger). \end{aligned} \quad (\text{A8})$$

Here we defined

$$\begin{aligned} \xi_{\lambda,\mathbf{G}}^\sigma(\mathbf{k}) &= f_D(|\mathbf{k} + \mathbf{G}|)\xi_0^D(\mathbf{k})P_{\nu,\lambda}^D(\mathbf{k} + \mathbf{G}), \quad \bar{\nu} = D, \\ \xi_{\lambda,\mathbf{G}}^\nu(\mathbf{k}) &= if_Q(|\mathbf{k} + \mathbf{G}|)|\mathbf{k} + \mathbf{G}|\bar{R}\xi_0^Q(\mathbf{k})P_{\nu,\lambda}^Q(\mathbf{k} + \mathbf{G}), \\ \bar{\nu} &= Q, \end{aligned} \quad (\text{A9})$$

and

$$\Xi_{\mathbf{G},\mathbf{G}'}^{\lambda\lambda'}(\mathbf{k}) = \sum_{\bar{\nu}} \omega_{\bar{\nu}} \xi_{\lambda',\mathbf{G}'}^{\nu*}(\mathbf{k}) \xi_{\lambda,\mathbf{G}}^\nu(\mathbf{k}), \quad (\text{A10})$$

with the LM coupling parameter

$$\xi_0^{\bar{\nu}}(\mathbf{k}) = \sqrt{\frac{2\pi\Lambda_{\bar{\nu}}}{\omega_{p,\mathbf{k}}}} \quad (\text{A11})$$

and polarization tensors

$$\begin{aligned} P_{\nu,\lambda}^D(\mathbf{k}) &= \hat{e}_\nu \cdot \hat{e}_\lambda, \\ P_{\nu,\lambda}^Q(\mathbf{k}) &= \frac{1}{2}[\chi_\nu : \hat{e}_k \hat{e}_\lambda + \hat{e}_\lambda \hat{e}_k]. \end{aligned} \quad (\text{A12})$$

Here χ_ν are the unit tensors for the quadrupoles. The unit vector $\hat{e}_\lambda$ that specifies the photon polarization depends on $\mathbf{k}$. Finally, we also introduce the form factors

$$\begin{aligned} f_D &= \frac{3}{(k\rho_j)^3} [\sin(k\rho_j) - k\rho_j \cos(k\rho_j)], \\ f_Q &= \frac{9}{(k\rho_j)^3} [\text{Si}(k\rho_j) - \sin(k\rho_j)] \end{aligned} \quad (\text{A13})$$

that take into account the finite size of the nanoparticles; $\text{Si}(x)$ is the sine integral function.

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