# Interband exciton Raman scattering of light in semiconductors

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A theory is developed of interband exciton Raman scattering (RS) of light in semiconductors with both dipole-forbidden and dipole-allowed transitions between the valence and conduction bands. When the semiconductor is excited by light whose frequency is in the region of the intrinsic absorption, the scattered-light spectrum has a series of discrete lines corresponding to excitation, in the crystal, of discrete-spectrum exciton states with a total wave vector $\mathbf{K}\approx 0$. The frequencies of these lines are determined by the relation $\omega_s(n)=\omega_l-E_{ex}(n)/\hbar$, where $\omega_l$ is the frequency of the exciting light, and $E_{ex}(n)$ is the energy of the exciton state with principal quantum number $n=1,2,\ldots$. For semiconductors with allowed transition, the $\omega_s(1)$ line is forbidden by the selection rules. At primary light frequencies determined from the positions of the upper conduction bands and the lower valence bands, the exciton RS of light becomes resonant.

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## 1. INTRODUCTION

Illumination of a semiconductor crystal can cause, besides scattering of the light with participation of phonons, also scattering processes in which all the transitions are electronic—this is the so-called electron Raman scattering (RS) of light. Electron RS is a perturbation-theory second-order process. There are therefore three types of electronic states—initial, intermediate, and final. With the exception of the case of resonant scattering of light, the intermediate electronic state is virtual. In intraband electron RS, the initial and final electronic states lie in the same energy band (see, e.g., Ref. 1). In interband electron RS, the initial and final electronic states lie in different bands. Obviously, interband electron RS is possible only when the crystal is illuminated with light at a frequency exceeding the width of the forbidden band. Depending on the position of the intermediate state, two cases can be separated: when the initial, intermediate, and final electronic states lie in different energy bands, and when the intermediate state belongs to the same energy band as the final electronic state. In the former case the transition from the initial to the intermediate electronic states and the transition from the intermediate to the final electronic states are interband transitions. These light scattering processes will be called processes of type $A$. In the second case the transition from the initial to the intermediate state is interband, and the transition from the intermediate to the final electronic state is intraband. These light-scattering processes will be called processes of type $B$. The Feynman diagrams for the amplitudes of the scattering processes of type $A$ and $B$ are shown in Fig. 1.

In order for the electron transitions in light scattering of type $A$ to be dipole-allowed, it is necessary (but not sufficient) that the irreducible representations of the crystal symmetry group for the bands of the initial and final electronic states have one parity relative to the inversion operation, and the irreducible representation for the intermediate electron state band have the opposite parity. In this case, the interband transition for a scattering process of type $B$ will be dipole-forbidden. One can therefore expect the contribution made to the cross section for light scattering by processes of type $B$ to be smaller than the contribution of the type-$A$ process. If the irreducible representations of the symmetry group of the crystal for the bands of the initial and final states are such that a transition between these bands is dipole-allowed, then, independently of the symmetry of the band of the intermediate electronic states, at least one transition in type-$A$ scattering will be dipole forbidden, whereas in the scattering of type $B$ the interband electron transition will be dipole allowed. In this case the scattering of type $B$ can make a larger contribution to the light-scattering cross section than the contribution of processes of type $A$.

The contribution of the processes of type-$A$ light scattering with excitation of electronic states of the continuous spectrum to the cross section of the interband electron RS was investigated in Refs. 2–6, while the contribution of processes of type $B$ was investigated in Ref. 7. Studies were made[8-10] of interband electron RS in semiconductors placed in a strong magnetic field, with account taken of only type-$B$ scattering processes with excitation of electronic states of the continuous spectrum. A light-scattering process was considered[2-10] in which the initial electronic state is an elec-

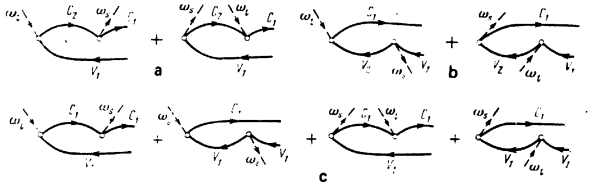

FIG. 1. Diagrams a and b describe two possible electron RS processes of type $A$: a) initial state—electron in valence band $V_1$, intermediate state—electron in the upper conduction band $C_2$, final state—electron in the lower conduction band $C_1$; b) intermediate state-electron in band $C_1$, hole in lower valence band $V_2$, final state—electron in band $C_1$, hole in band $V_1$. Diagrams c describe the type-$B$ light-scattering process.

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tron in the valence band, and the final state is an electron in the lower conduction band. Since the intermediate and final electronic states were taken to be states of an unbound electron-hole pair, belonging to the continuous electron spectrum of the crystal, the spectrum of the scattered light spans over a broad frequency band[1)]

$$0<\omega_s\leqslant\omega_l-E_g/\hbar, \qquad (1.1)$$

where $E_g$ is the width of the forbidden band, and $\omega_l$ and $\omega_s$ are respectively the frequencies of the primary and secondary light.

In interband electron RS, transitions are also possible to states of a discrete exciton spectrum. By virtue of the momentum conservation law, these excitonic states, if the photon wave vectors are neglected, should have a summary wave vector $\mathbf{K}=0$. It is clear that transitions to excitonic states of the discrete spectrum with $\mathbf{K}=0$ should correspond in the scattered-light spectrum to a series of discrete lines with frequencies $\omega_s>\omega_l-E_g/\hbar$. The light-scattering process with excitation of discrete excitonic states with $K=0$ will hereafter be called interband exciton RS.

The possibility of a manifestation of exciton effects in the interband electron RS was indicated in Refs. 2 and 4. The first attempt to estimate the contribution of the light scattering processes of type $B$ to the cross section of exciton RS was made in Ref. 12, and the contribution of processes of light scattering of type $A$ was not investigated at all. In the present paper we develop a theory of interband exciton RS with account taken of light-scattering processes of type $A$ and $B$. The contribution of the light-scattering processes of type $B$, for semiconductors with dipole-allowed transitions between the valence band and the conduction band is calculated in Sec. 2. In Secs. 3 and 4, using the semiconductor crystal $Cu_2O$ as an example, we investigate the interband exciton RS in semiconductors with forbidden transition.

## 2. EXCITON RS IN THE CASE OF ALLOWED TRANSITIONS

In second-order perturbation theory, the cross section of interband electron RS can be represented in the form

$$\frac{d^2\sigma}{d\omega_s\,d\Omega}=\frac{e^4\hbar\omega_s n(\omega_s)}{m_0^4c^4\omega_l n(\omega_l)}\sum_f\Big|\sum_r\Big\{\frac{\langle f|\mathbf{e}_s\mathbf{p}|r\rangle\langle r|\mathbf{e}_l\mathbf{p}|0\rangle}{\hbar\omega_l-E_{ex}(r)}-\frac{\langle f|\mathbf{e}_l\mathbf{p}|r\rangle\langle r|\mathbf{e}_s\mathbf{p}|0\rangle}{\hbar\omega_l+E_{ex}(r)}\Big\}\Big|^2\delta(\hbar\omega_l-\hbar\omega_s-E_{ex}(f)), \qquad (2.1)$$

where $\Omega$ is the solid angle, $m_0$ is the mass of the free electron, $n(\omega)$ is the refractive index, $p$ is the momentum operator, $\mathbf{e}_l$ and $\mathbf{e}_s$ are respectively the polarization vectors of the primary and scattered light; $|0\rangle$, $|r\rangle$, and $|f\rangle$ are the wave functions of the ground (initial), intermediate, and final electronic states of the semiconductor. The states $r$ and $f$ can belong to the discrete as well as to the continuous exciton spectrum of the crystal. In addition, the states $r$ and $f$ belong to either one exciton series (scattering process of type $B$) or to different exciton series produced by different production bands or by different valence bands.

If the wave vectors of the photon are neglected, then by virtue of the momentum conservation law the summary wave vector $\mathbf{K}$ of the excitonic state $r$ is zero, and the same holds for the state $f$. We shall assume the excitonic states to be hydrogen-like. Then the energy of the excitonic state of the discrete spectrum with $\mathbf{K}=0$ and with principal quantum number $n$ is equal to

$$E_{ex}(n)=E_g-e^4\mu/2\hbar^2\varkappa_0n^2, \qquad (2.2)$$

where $n=1,2,\ldots$, $\varkappa_0$ is the static dielectric constant of the crystal. For excitonic states of the continuous spec-spectrum with $\mathbf{K}=0$ and with relative-motion wave vector $k$, the energy $E_{ex}(k)$ is

$$E_{ex}(k)=E_g+\hbar^2k^2/2\mu. \qquad (2.3)$$

We consider now the scattering of light with excitation of excitonic states of the discrete spectrum with $\mathbf{K}=0$, i.e., $|f\rangle=|n,l,m\rangle$. From the energy conservation law it follows that the frequency of the scattered light takes on a discrete set of values

$$\omega_s=\omega_s(n)\equiv\omega_l-E_{ex}(n)/\hbar, \qquad (2.4)$$

where $n=1,2,\ldots$. We investigate the exciton RS in semiconductors with dipole-allowed transition between the upper valence band and the lower conduction band. In the course of type-$B$ light scattering, the final and intermediate excitonic states $f$ and $r$ belong to the exciton series produced by these bands. The matrix element $\langle n,l,m|\mathbf{p}|0\rangle$ of the momentum operator between the ground state of the crystal $|0\rangle$ and the exciton state with $\mathbf{K}=0$ is

$$\langle n,l,m|\mathbf{p}|0\rangle=\mathbf{p}_{cv}\left(\frac{V_0}{\pi a^3n^3}\right)^{1/2}\delta_{l,0}\delta_{m,0}, \qquad (2.5)$$

where $V_0$ is the volume of the crystal, $a=\hbar^2\varkappa_0/e^2\mu$ is the Bohr radius of the exciton, and $\mathbf{p}_{cv}$ is the interband matrix element of the momentum operator. As seen from (2.5), the intermediate (virtual) exciton state $|r\rangle=|n,l,m\rangle$ should be a state of the $s$ type, i.e., $|r\rangle=|n,0,0\rangle$.

For the matrix element $\langle f|\mathbf{e}\cdot\mathbf{p}|r\rangle$ of the transition from the excitonic state $|n',l',m'\rangle$ into the excitonic state $|n,l,m\rangle$ we have[13]

$$\langle n,l+1,m|\mathbf{ep}|n',l',m'\rangle=\frac{iam_0(E_{ex}(n)-E_{ex}(n'))}{i\hbar[(2l+3)(2l+1)]^{1/2}}\times\{e_z\delta_{m,m'}[(l+1)^2-m^2]^{1/2}+(e_x-ie_y)\delta_{m,m'+1}[2^{-1}(l+m'+2)(l+m'+1)]^{1/2}-(e_x+ie_y)\delta_{m,m'-1}[2^{-1}(l-m'+2)(l-m'+1)]^{1/2}\}R^{nl+1}_{n'l}\delta_{l',l}, \qquad (2.6)$$

where $e_x$, $e_y$, and $e_z$, are the $x$, $y$, and $z$ projections of the vector $\mathbf{e}$,

$$R^{nl}_{n'l'}=\int dr\,r^3R_{nl}(r)R_{n'l'}(r), \qquad (2.7)$$

$R_{nl}(r)$ is the hydrogen radial wave function. A general expression and a table of the values of $R^{nl}_{n'l'}$ are given in Ref. 13.

It follows from (2.4) and (2.6) that in a type-$B$ light-scattering process the final excitonic state, after emission of a secondary light photon, is an excitonic state of $p$-type with $\mathbf{K}=0$. It can be shown that for semiconductors with dipole-allowed transitions this statement remains valid also for type-$A$ light-scattering processes. Consequently, in the scattered-light spectrum, lines with frequencies $\omega_s(n \geqslant 2)$ [see formula (2.4)] are allowed and correspond to light scattering with excitation of $p$-type excitonic states of the discrete spectrum with $\mathbf{K} = 0$, while the line $\omega_s(1)$ is forbidden by the selection rules.

We calculate now the integral scattering cross section for the line $\omega_s(n)$, when the primary radiation has a polarization $\mathbf{e}_l$, and the scattered light a polarization $\mathbf{e}_s$. Substituting (2.5) and (2.6) in (2.1) and taking into account only the sum over the intermediate states of the discrete exciton spectrum, a sum shown by analysis to make the principal contribution at not very large $n$, we obtain

$$\frac{d\sigma(n)}{d\Omega}=\frac{C_n}{3\pi}\left(\frac{e^2}{\hbar c}\right)^2 V_0\frac{n(\omega_s)\omega_s}{n(\omega_l)\omega_l a m_0^2c^2}$$
$$\times\left\{|\mathbf{e}_l\mathbf{p}_{cv}|^2\left(\frac{\Delta E}{\hbar\omega_l-E_g}\right)^2+|\mathbf{e}_l\mathbf{p}_{cv}|^2\left(\frac{\Delta E}{\hbar\omega_l}\right)^2\right.$$
$$\left.-2\frac{(\Delta E)^2}{(h\omega_l-E_g)\hbar\omega_l}\operatorname{Re}(\mathbf{e}_s\mathbf{e}_l^*)(\mathbf{e}_l\mathbf{p}_{cv})(\mathbf{e}_s^*\mathbf{p}_{cv}^*)\right\}, \tag{2.8}$$

where $\Delta E = \mu e^4/2\hbar\varkappa_0^2$ is the exciton binding energy. In the derivation of (2.8) we have assumed that $\hbar\omega_l - E_g \gg \Delta E$,

$$C_n=\left|\sum_{m=1}^{\infty}m^{-3/2}(m^{-2}-n^{-2})R_{m0}{}^{n1}\right|^2. \tag{2.9}$$

For the frequency region $\hbar\omega_l - E_g \ll \hbar\omega_l$, expression (2.8) coincides with the result of Ref. 12. The numbers $C_n$ determine the relative intensity of the lines $\omega_s(n)$. Using only the first eight terms in the sum (2.9), we obtain $C_2 = 0.85$ and $C_3 = 0.38$.

We now estimate numerically the integral light-scattering cross section (2.9) for the CdS crystal. It is known that in CdS there are observed hydrogenlike excitonic states. These are excitons of series $A$, produced by the conduction band $\Gamma_7$ and the valence band $\Gamma_9$. For unpolarized light, an electron transition from the valence band $\Gamma_9$ to the conduction band $\Gamma_7$ is dipole-allowed, so that when the crystal is illuminated at a frequency $\omega_l > E_g/\hbar$, a series of lines should be observed in the spectrum of the scattered light, with frequencies $\omega_s$ $(n \geqslant 2)$ determined by formula (2.4) and corresponding to excitation in the crystal of excitonic states of the $p$-type of series $A$. The width of the forbidden band is $E_g = 2.55$ eV, so that at the primary-light frequency from the interval 3–4.5 eV, the corresponding line frequency $\omega_s(2)$ lies in the interval 0.5–2 eV. For this frequency region the value of $V_0^{-1}d\sigma(2)/d\Omega$ lies correspondingly in the interval $10^{-6}$–$10^{-7}$ $\text{cm}^{-1}\cdot\text{sr}^{-1}$.

We have considered above only the contribution of type-$B$ light scattering processes to the cross section of the exciton RS. It follows from group theory that if the light scattering is accompanied by excitation of excitonic states produced by the valence band and the conduction band, between which the transition is dipole-allowed, at least one of the electron transitions in the type-$A$ scattering process will be forbidden. Therefore the contribution made to the light-scattering by processes of type $A$ is possibly smaller than that of processes of type $B$.

## 3. INTERBAND EXCITON RS OF TYPE $A$ IN $Cu_2O$

In the present section, using the cubic crystal $Cu_2O$ as an example, we consider the calculation of the contributions of processes of type $A$ to the cross section of exciton RS in semiconductors with forbidden transition between the valence band and the conduction band. There are several exciton series in the $Cu_2O$ crystal (see the reviews, Refs. 14 and 15). The band structure of $Cu_2O$ at $\mathbf{k} = 0$ is shown in Fig. 2. We consider the scattering of light with excitation of excitonic states of the "yellow" series. The excitonic states of the yellow series are produced by the conduction band with symmetry[2)] $\Gamma_6^+$ and valence band $\Gamma_7^+$ (Refs. 16 and 17). The excitonic states of $s$-type (it will be shown below that these are the only yellow-series excitonic states in which a transition in the type-$A$ scattering processes is allowed) have a symmetry determined by the direct product of the irreducible representations $\Gamma_1^+ \times \Gamma_6^+ \times \Gamma_7^+ = \Gamma_{25}^+ + \Gamma_2^+$. The state $\Gamma_{25}^+$ corresponds to a triplet excitonic state, and the singlet excitonic state has the symmetry[3)] $\Gamma_2^+$.

In the exciton RS process, the transition to excitonic states of the yellow series is possible in second-order perturbation theory only via excitonic states produced by the conduction band $\Gamma_6^+$ and the lower valence bands, or else via excitonic states produced by the valence band $\Gamma_7^+$ and the upper conduction bands. Let the intermediate band have the symmetry $\Gamma_i$. It follows from group theory that only at $\Gamma_i = \Gamma_8^{-1}$ are a transition between the valence band $\Gamma_7^+$ and the band $\Gamma_i$ and a transition between the conduction band $\Gamma_6^+$ and the band $\Gamma_i$ simultaneously dipole-allowed. A symmetry $\Gamma_8^-$ is possessed, e.g., by the upper conduction band, which together with the valence band $\Gamma_7^+$ forms the "blue" exciton series[14] (see Fig. 2). The process of light scattering with excitation of excitonic states of the yellow series via an intermediate band with symmetry $\Gamma_i$ different from $\Gamma_8^-$ will contain at least one forbidden transition. We shall consider below the process of light scattering with transition only via intermediate excitonic states of the blue series.

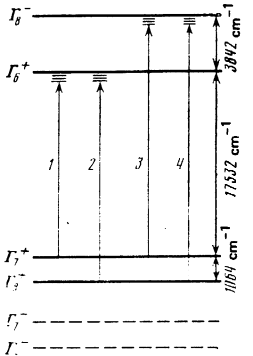

FIG. 2. Diagram of band structure of $Cu_2O$ at $\mathbf{k} = 0$.[14] The number 1 denotes the electron transitions into excitonic states of the yellow series, the number 2—into excitonic states of the green series, 3—into excitonic states of the blue series, 4—into excitonic states of the dark blue series. The notation for the irreducible representations corresponds to the double cubic group.

Since the transition from the band $\Gamma_7^+$ to the band $\Gamma_8^-$ is dipole-allowed, a transition from the ground state $\Gamma_1^+$ of the crystal is possibly only to an $s$-type excitonic state of the blue series [see (2.5)]. The symmetry of an $s$-type state of the blue series is determined by the direct product

$$\Gamma_1^+\times\Gamma_7^+\times\Gamma_8^-=\Gamma_{12}^-+\Gamma_{15}^-+\Gamma_{25}^-. \tag{3.1}$$

It follows from group theory that a transition from $\Gamma_1^+$ is dipole-allowed only into an excitonic state that transforms in accordance with the irreducible three-dimensional representation $\Gamma_{15}^{-1}$. A state with symmetry $\Gamma_{15}^{-1}$ is a triplet excitonic state. A transition from the intermediate state $\Gamma_{15}^-$ of the blue series is allowed only to the triplet excitonic state $\Gamma_{25}^+$ of the yellow series. Thus, in the interband exciton RS of type $A$ in $Cu_2O$, the intermediate and final excitonic states are $s$-type states. The excitonic states of the blue series have a symmetry $\Gamma_{15}^-$, and the final excitonic states of $s$-type of the yellow series have the symmetry $\Gamma_{25}^+$. In contrast to the exciton RS in semiconductors with dipole-allowed transition between the valence band the conduction band, which form the exciton series, in the case of a dipole-forbidden transition the line $\omega_s(1)$ in the scattered-light spectrum is allowed by the selection rules.

The matrix element of the momentum operator for the dipole-allowed transition from the ground state of the crystal into an $s$-type excitonic state with principal quantum number $n$ is given by expression (2.5). The matrix element of the momentum operator for the dipole-allowed transition from the excitonic state $n', l', m'$ of the blue series into the excitonic state $n, l, m$ of the yellow series can be obtained by using the method of Ref. 19:

$$\langle 1; n,l,m|\mathbf{p}|2; n',l',m'\rangle=\mathbf{p}_{12}(a_1^3a_2^3)^{-1/2}\delta_{l,l'}\delta_{m',m}\int dr\, r^2R_{nl}(a_1^{-1}r)R_{n'l}(a_2^{-1}r), \tag{3.2}$$

where $\mathbf{p}_{12}=\langle 1|\mathbf{p}|2\rangle$, $|1\rangle$ and $|2\rangle$ are respectively the Bloch functions of the bands $\Gamma_6^+$ and $\Gamma_8^-$ at $\mathbf{k}=0$, and $a_1$ and $a_2$ are the Bohr radii of the excitons of the yellow and blue series. Substituting (3.2) and (2.5) in (2.1) and recognizing that the intermediate excitonic states have the symmetry $\Gamma_{15}^-$ and the final excitonic states the symmetry $\Gamma_{25}^+$, we obtain for the frequency-integrated cross section of the line the expression

$$\frac{d\sigma}{d\Omega}=\frac{1}{2\pi}\left(\frac{e^2}{\hbar c}\right)^2\frac{V_0\omega_s n(\omega_s)\mu_2}{\omega_l n(\omega_l)m_0a_2}\frac{(E_{g2}-E_{g1})E_{g2}}{\Delta E_2 m_0c^2}$$
$$\times f_{02}f_{12}\left|\sum_{m=1}^{\infty}\frac{A_m^n}{m^{3/2}}\left(\frac{\Delta E_2}{\hbar\omega_l-E_{ex}^{(2)}(m)}-\frac{\Delta E_2}{\hbar\omega_s+E_{ex}^{(2)}(m)}\right)\right|^2 Z, \tag{3.3}$$

where $\mu_2$, $\Delta E_2$, $E_{ex}^{(2)}(n)$ are the reduced mass, binding energy, and energy of the excitonic state of the blue series,

$$f_{ji}=\frac{2|\mathbf{p}_{ij}|^2}{m_0(E_{gi}-E_{gj})} \tag{3.4}$$

is the oscillator strength of the transition from the band $j$ to the band $i$,

$$A_m^n=(a_1^3a_2^3)^{-1/2}\int dr\, r^2R_{n0}(a_1^{-1}r)R_{m0}(a_2^{-1}r). \tag{3.5}$$

The factor $Z$ in (3.3) determines the angular dependence of the light-scattering cross section:

$$Z=1-2(e_{sx}^2e_{lx}^2+e_{sy}^2e_{ly}^2+e_{sz}^2e_{lz}^2)+(\mathbf{e}_s\mathbf{e}_l)^2. \tag{3.6}$$

If the Bohr radii of the excitons of the yellow and blue series were approximately equal ($a_1\approx a_2$), then by virtue of the orthogonality of the radial functions $R_{nl}(r)$ we would have $A_m^n=\delta_{m,n}$. It appears, however, that $a_1\neq a_2$ (Ref. 14), therefore $A_m^n\neq 0$ at $n\neq m$.

As is easily seen from (3.3), when the energy of the primary photon is equal to the energy of one of the exciton states of the blue series, i.e.,

$$\omega_l=E_{ex}^{(2)}(n), \tag{3.7}$$

where $n=1,2,\ldots$, the energy denominator in (3.3) vanishes and the light scattering becomes resonant. When condition (3.7) is satisfied, the intensities of all the lines $\omega_s(n)$ increase resonantly. The reason is that $A_m^n\neq 0$ at $n\neq m$.

We obtain now numerical estimates of the cross section (3.3). In $Cu_2O$ we have $E_{g1}=2.17$ eV and $E_{g2}=2.65$ eV.[14] Since the Rydberg constant for the yellow series is double the Rydberg constant for the blue series,[14] we can put for numerical estimates $a_2=2a_1$. For a frequency $\hbar\omega_l=4$ eV (far from the resonant $\hbar\omega_l\approx 2.6$ eV) and $h_s(1)=1.93$ eV we have

$$V_0^{-1}d\sigma(1)/d\Omega\sim 10^{-6}f_{02}f_{12}\,\text{cm}^{-1}\cdot\text{sr}^{-1}.$$

The transitions $0\to 2$ and $2\to 1$ are dipole-allowed, and therefore apparently the oscillator strengths of these transitions $f_{02}f_{12}\gtrsim 1$, and then $V_0^{-1}d\sigma/d\Omega\gtrsim 10^{-6}$ cm$^{-1}$ $\cdot$ sr$^{-1}$.

We investigate, in one particular case, the polarization of the scattered light. Let the primary light propagate along a fourfold axis $C_4$ and let it be linearly polarized along the vector $\mathbf{e}_l$. Let this axis be the $y$ axis of a Cartesian coordinate system $x, y, z$. The axes $x$ and $z$ are directed along the two other $C_4$ axes. We consider "forward" scattering (the same will hold true for "backward" scattering). One of the linearly independent polarization vectors of the scattered light $\mathbf{e}_s'$ is chosen to be parallel and the second vector $\mathbf{e}_s''$ perpendicular to $\mathbf{e}_l$. The degree of linear polarization of the scattered light is determined by the relation

$$\xi=[W(\mathbf{e}_s')-W(\mathbf{e}_s'')]/[W(\mathbf{e}_s')+W(\mathbf{e}_s'')], \tag{3.8}$$

where $W(\mathbf{e})$ is the probability of emission of scattered light with polarization $\mathbf{e}$. From (3.3) and (3.6) we obtain

$$\xi=\cos 4\theta, \tag{3.9}$$

where $\theta$ is the angle between the vector $\mathbf{e}_l$ and the $z$ axis. It follows from (3.9) that $\xi=0$ at $\theta=(2n+1)\pi/8$, where $n=0,1,\ldots,7$, i.e., the scattered light is unpolarized. If $\theta=(2n+1)\pi/4$, where $n=0,1,2,3$, then $\xi=-1$, i.e., the light is fully linearly polarized in the direction $\mathbf{e}_s''$ perpendicular to $\mathbf{e}_l$. If $\theta=n\pi/2$, where $n=0,1,2,3$ then $\xi=1$, i.e., the scattered light is completely linearly polarized along the polarization direction $\mathbf{e}_l$ of the primary light.

We have considered above exciton RS with excitation of the excitonic states of the yellow series via intermediate states of the blue series. Transitions via the excitonic states of other series can be similarly taken into account. However, the contribution of these processes to the light scattering cross section is probably small, since one of the electron transitions is forbidden, with the possible exception of the case when the condition (3.7) of resonance with the corresponding band is satisfied. One can consider also light scattering with excitation of excitonic states of other series, e.g., the "green" series. In this case it follows from group theory that only electronic transitions via intermediate bands with symmetry $\Gamma_6^-$ and $\Gamma_8^-$ into excitonic states of the yellow series are dipole-allowed.

## 4. TYPE-B SCATTERING PROCESS IN Cu$_2$)

We estimate now the contribution of the type-*B* scattering processes in a Cu$_2$O. Using the results of Refs. 17, 19, and 20, we can express the matrix element of the momentum operator, for a transition from the ground state of the crystal into a hydrogenlike excitonic state with quantum indices $n, l, m$ and with a total wave vector K = 0, in the form

$$\langle n,l,m|(\mathbf{p})_\alpha|0\rangle=\hbar\left(\frac{V_0}{a^3}\right)^{1/2}\sum_\beta M_{\alpha\beta}\frac{\partial}{\partial x_\beta}\Phi^*_{nlm}\quad (r=0), \tag{4.1}$$

where $\alpha, \beta = 1, 2, 3$ and $x_1 = x$, $x_2 = y$, $x_3 = z$. The tensor $M_{\alpha\beta}$ is defined by the expression

$$M_{\alpha\beta}=\frac{1}{m_0}\sum_j{}'\left\{\frac{(\mathbf{p}_{cj})_\alpha(\mathbf{p}_{jv})_\beta}{E_c-E_j}-\frac{(\mathbf{p}_{cj})_\beta(\mathbf{p}_{jv})_\alpha}{E_j-E_v}\right\}, \tag{4.2}$$

where $\mathbf{p}_{ij} = \langle i|\mathbf{p}|j\rangle$ and $E_j$ is the energy position of the bottom of the $j$-band.

The concrete form of the tensor $M_{\alpha\beta}$ is determined by the symmetry of the valence band and of the conduction band; $\Phi_{nlm}(r) = R_{nl}(r)Y_{lm}(\vartheta, \varphi)$ is a hydrogenlike wave function of the state $n, l, m$. The derivative of the function $\Phi_{n,l,m}$ along the direction e is different from zero at the origin ($r = 0$) only for wave functions of $p$-type states

$$\mathbf{e}\nabla\Phi_{n10}(0)=\frac{1}{a}\left(\frac{n^2-1}{3\pi n^5}\right)^{1/2}e_z, \tag{4.3}$$

$$\mathbf{e}\nabla\Phi_{n1\pm1}(0)=\frac{1}{a}\left(\frac{n^2-1}{6\pi n^5}\right)^{1/2}(e_x\pm ie_y). \tag{4.4}$$

Just as in Sec. 3, we consider light scattering with excitation of excitonic states of the yellow series. In the type-*B* light-scattering process, the intermediate (virtual) excitonic states also belong to the yellow series. As follows from (4.1), an intermediate excitonic state should be of $p$-type. The $p$-type excitonic states of the yellow series have a symmetry determined by the direct product $\Gamma_{15}^-\times\Gamma_6^+\times\Gamma_7^+=\Gamma_{15}^-\times\Gamma_2^++\Gamma_{15}^-\times\Gamma_{25}^+$. From the selection rules for the matrix element of the momentum operator it follows that a transition from the ground state of the crystal $\Gamma_1^+$ is allowed only into a $p$-type excitonic state with symmetry $\Gamma_{15}^-\times\Gamma_{25}^+$—this is a triplet excitonic state. The basis functions for the three-dimensional irreducible representation of $\Gamma_{25}^+$ are functions that transform like $\varphi_1 = yz$, $\varphi_2 = xz$, and $\varphi_3 = xy$. Using this, it can be shown that for transitions into triplet excitonic states with wave functions that transform like $\varphi_i$, the matrices $M_{\alpha\beta}^{(i)}$ (4.2) are equal to

$$M_{\alpha\beta}^{(1)}=A\begin{pmatrix}0&0&0\\0&0&1\\0&1&0\end{pmatrix},\quad M_{\alpha\beta}^{(2)}=A\begin{pmatrix}0&0&1\\0&0&0\\1&0&0\end{pmatrix},\quad M_{\alpha\beta}^{(3)}=A\begin{pmatrix}0&1&0\\1&0&0\\0&0&0\end{pmatrix}, \tag{4.5}$$

$$A=m_0E_gx_{cv}^2\hbar^{-2}, \tag{4.6}$$

where $x_{cv}^2$ is a quantity of the order of the square of the atomic radius. For Cu$_2$O we have $x_{cv}\approx 1.5$ Å (Ref. 15).

We calculate now the contribution made to the light-scattering cross section by type-*B* processes with excitation of excitonic states of $s$-type. The transition from a $p$-state with symmetry $\Gamma_{15}^-\times\Gamma_{25}^+$ is allowed only into states of $s$-type with symmetry $\Gamma_{25}^+$. Substituting (4.1)–(4.6) and (2.6) in the expression for the light-scattering cross section (2.1) and neglecting transitions via the states of the continuous exciton spectrum, we obtain for the frequency-integrated scattering cross section of the $\omega_s(n)$ line the expression

$$d\sigma(n)/d\Omega=V_0A(\omega_l)B_s(n)Z, \tag{4.7}$$

where $n = 1, 2, \ldots$ and the coefficients $A(\omega_l)$ and $B_s(n)$ are given by

$$A(\omega_l)=\frac{1}{8\pi}\left(\frac{e^2}{\hbar c}\right)^2\left(\frac{x_{cv}}{a}\right)^4\frac{E_g^2n(\omega_s)\omega_s}{a\Delta E\mu c^2n(\omega_l)\omega_l}\left(\frac{\Delta E}{\hbar\omega_l-E_g}-\frac{\Delta E}{\hbar\omega_l}\right)^2, \tag{4.8}$$

$$B_s(n)=\left|\sum_{m=2}^{\infty}\left(\frac{m^2-1}{m^5}\right)^{1/2}(m^{-2}-n^{-2})R_{n0}^{m1}\right|^2. \tag{4.9}$$

The quantity $Z$ is defined by expression (3.6). Using only the first eight terms in (4.9) yields $B_s(1) = 0.33$ and $B_s(2) = 0.014$.

The transitions possible from $p$-type intermediate excitonic states are those into $d$-type states. The scattering processes of type *B* with excitation of excitonic states of type-$d$ contribute only to the intensities of the lines $\omega_s(n)$ with $n \geqslant 3$.

We present now numerical estimates of the cross section (4.7). If the primary-light photon energy is $\hbar\omega_l = 4$ eV, then $V_0^{-1}d\sigma(1)/d\Omega\sim 10^{-1}$ cm$^{-1}\cdot$sr$^{-1}$. A comparison of this value of the contribution of the type-*B* light-scattering processes to the cross section of the exciton RS with the contribution of the type-*A* scattering processes for semiconductors with forbidden transitions between the valence band and the conduction band shows that the type-*A* light-scattering processes make the main contribution to the cross section of the exciton RS.

We have not taken into account in this study polariton effects, i.e., we have assumed that excitons and photons are independent quasiparticles. This is valid when the oscillator strength of the exciton transition is weak (e.g., as in the Cu$_2$O crystal, in which a transition to the excitonic state of the yellow series is forbidden). When the oscillator strength of the exciton transition is large enough, then the final and intermediate states in the considered process of light scattering must be taken to be polariton states. Allowance for the polariton effects, in all probability, leads to a certain change in the line positions in the scattered-light spectrum, depending on the direction of the scattering, but to estimate the cross section of the interband exciton RS we can nonetheless use formula (2.1).

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1) It should be noted that the hot-luminescence spectrum also falls in the frequency region (1.1).[11]

2) The notation employed for the irreducible representation corresponds to the double cubic group.

3) The angular dependence of the absorption-spectrum line corresponding to a transition to the excitonic ls state agrees with the symmetry $\Gamma_{25}^{+}$ for the *ls* state.[18]

[1] M. V. Klein, in: Light Scattering in Solids, M. Cardona, ed., Springer, 1975.

[2] R. J. Elliot and R. Loudon, Phys. Lett. **3**, 189 (1963).

[3] S. S. Jha, Nuovo Cim. **63B**, 331 (1969).

[4] E. Burstein, D. L. Mills, and R. F. Wallis, Phys. Rev. **B4**, 2429 (1971).

[5] S. Srivastava and K. Arya, Phys. Rev. **B8**, 667 (1973).

[6] R. Enderlein, Phys. Stat. Sol. (b) **70**, 263 (1975).

[7] A. V. Gol'tsev, I. G. Lang, and S. T. Pavlov Fiz. Tverd. Tela (Leningrad) **20**, 2542 (1978) [Sov. Phys. Solid State **20**, 1473 (1978)].

[8] R. F. Wallis and D. L. Mills, Phys. Rev. **B2**, 3312 (1970).

[9] G. K. Vlasov, Fiz. Tverd. Tela (Leningrad) **17**, 3385 (1975) [Sov. Phys. Solid State **17**, 2215 (1975)].

[10] A. V. Goltsev, I. G. Lang, and S. T. Pavlov, Phys. Stat. Sol. (b) **94**, 37 (1979).

[11] A. V. Gol'tsev, I. G. Lang, and S. T. Pavlov, Zh. Eksp. Teor. Fiz. **75**, 279 (1978) [Sov. Phys. JETP **48**, 139 (1978)].

[12] A. V. Gol'tsev, Fiz. Tverd. Tela (Leningrad) **22**, 2360 (1980) [Sov. Phys. Solid State **22**, 1373 (1980)].

[13] H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One- and Two- Electron Systems, Springer, 1958. Russ. transl. Fizmatgiz, 1960, p. 398.

[14] E. F. Gross, Usp. Fiz. Nauk **76**, 433 (1962) [Sov. Phys. Usp. **5**, 195 (1962)].

[15] R. S. Knox, Theory of Excitons, Academic, 1963.

[16] A. G. Zhilich, Vestnik LGU, ser. fiz. khim. **4**, No. 22, 5 (1959); 2, No. 10, 5 (1960).

[17] R. J. Elliott, Phys. Rev. **124**, 340 (1961).

[18] E. F. Gross and A. A. Kaplyanskiĭ, Fiz. Tverd. Tela (Leningrad) **2**, 379 (1960) [Sov. Phys. Solid State **2**, 353 (1960)].

[19] R. J. Elliott, Phys. Rev. **108**, 1384 (1957).

[20] R. J. Elliott and R. J. Loudon, J. Phys. Chem. Sol. 8, 382 (1959).

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