Selection rules for resonant hyper-Raman scattering of light in cuprous oxide with the participation of a 1*s* exciton of the yellow series

L. E. Zubkova, K. K. Ondriash, and K. A. Prokhorov

Institute of General Physics, Russian Academy of Sciences

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A relation from which the nonzero components of the hyperpolarizability tensor of crystals belonging to any point-symmetry group can be obtained by substituting appropriate Clebsch–Gordan coefficients is derived. The relation is used to find the selection rules for resonant hyper-Raman scattering (HRS) of light in a cuprous oxide crystal with participation of the 1*s* state of the yellow exciton series. It is shown that under the resonance conditions considered the HRS process is determined only by the off-diagonal components of the hyperpolarizability tensor. It is predicted that the forbidden vibration Γ_{12}^{-} should occur in the resonant HRS spectra of cuprous oxide and that the scattering lines corresponding to different *s* states should be amplified alternately as the probe radiation is tuned over the region of excitonic excitations.

1. INTRODUCTION

The optical spectrum of a cuprous oxide crystal contains four excitonic series at the absorption edge, and up to ten lines are observed in the most intense series, the yellow series.[1] For this reason Cu_2O is exceptionally interesting for studying nonlinear optical resonance phenomena. In particular, experimental investigations of resonant Raman scattering (RS) of light in cuprous oxide were performed in the 1970s after the advent of tunable dye lasers.[2–6] The resonant enhancement of RS lines which was observed in these experiments as the frequency of the probe radiation was tuned over the region of excitonic excitations made it possible to study in detail multiphonon relaxation of excitons of the yellow and green series.[2,3] In Refs. 4–6 it was observed that the scattering cross section in the Γ_{12}^{-} phonon, which is dipole-forbidden but allowed in the quadrupole approximation, is significantly larger when the exciting or scattered photon is in resonance with the *s* states of the yellow excitonic series. This increase in the scattering cross section was found to be in good agreement with the quadrupole mechanism, proposed by J. Birman in Refs. 7 and 8, for resonant Raman scattering. Two-photon absorption[9] and scattering by high-energy dipole-allowed excitons of the blue and violet series[10–11] have also been investigated in cuprous oxide.

Resonant hyper-Raman scattering of light could also be an effective method for studying electronic excitations of semiconductor materials and mechanisms of electron–photon and electron–phonon interactions. In an elementary HRS event two photons of the exciting radiation interact at the same time with the medium. This is especially important for investigating cuprous oxide crystals, in which only the two-photon dipole transition into the lower excitonic state is allowed. In addition, the selection rules for HRS are broader than for RS, which enables investigation of vibrations which are inactive in the RS and IR spectra.[13] Our approximate calculations showed that[14] under certain conditions in cuprous oxide the resonant HRS (RHRS) can be comparable in strength to resonant RS (RRS) and near-IR tunable lasers, developed in the last few years, make it possible to perform the corresponding experiments. It is thus of interest to make a detailed analysis of different aspects of RHRS in Cu_2O.

In this paper a group-theoretical study is made of resonant HRS in Cu_2O. Information about the band structure and symmetry properties of cuprous oxide, which are important for the further analysis, are briefly presented in Sec. 2. The selection rules for nonresonant HRS are derived in Sec. 3. The effect of two-photon resonance between the exciting radiation and the 1*s* state of the yellow exciton on the hyperpolarizability tensor of Cu_2O is studied in Sec. 4. Finally, the results obtained are discussed in Sec. 5.

2. BAND STRUCTURE AND SYMMETRY OF A Cu_2O CRYSTAL

Crystalline cuprous oxide is a direct-gap semiconductor with a band gap of 2.1720 eV at 2 K.[1] The unit cell of Cu_2O consists of four equivalent copper ions and two equivalent oxygen ions (Fig. 1), and the crystalline structure belongs to the symmetry space group O_h^4. It can be represented in the form of a cubic face-centered lattice and a cubic body-centered lattice, consisting of copper atoms and oxygen atoms, respectively, and displaced with respect to one another by one-fourth a lattice constant.[15,16]

Elliot made a fundamental theoretical investigation in Ref. 15 of the band structure of crystalline cuprous oxide and its symmetry properties. The highest valence band of Cu_2O is related to the 3*d* wave function of the copper atom and has Γ_{25}^{+} symmetry. The lowest conduction band is the Γ_1^{+} band, determined by a combination of the 4*s* and 3*s* wave functions of the copper and oxygen atoms. The significant spin–orbital interaction splits the upper valence band into two subbands

$$\Gamma_{25}^{+}\rightarrow\Gamma_7^{+}+\Gamma_8^{+}, \tag{1}$$

and changes the symmetry of the conduction band

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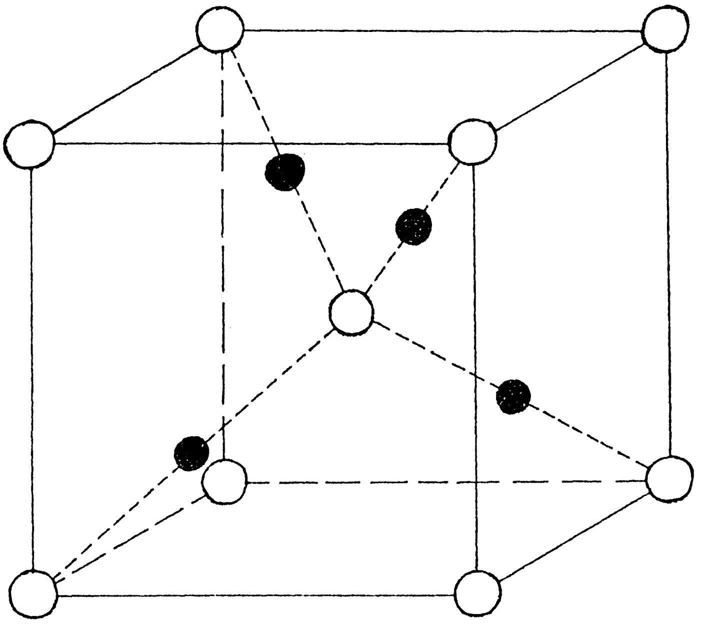

FIG. 1. Unit cell of Cu_2O: ●—Cu^+-ions; ○—O^{--}-ions.

$$\Gamma_1^+ \to \Gamma_6^+ . \qquad (2)$$

Thus, due to the spin–orbit interaction the quotient group of the space group of cuprous oxide is isomorphic not to the point group O_h but rather to the double point group O_h'.

The band structure of Cu_2O is displayed schematically in Fig. 2. The yellow and green excitonic series are formed with electronic transitions from the valence subbands Γ_7^+ and Γ_8^+, respectively, into the excitonic levels near the lowest conduction band Γ_6^+. The excitons of the blue and violet series are associated with electronic transitions from the same valence subbands into the top conduction band Γ_{12}^-. We note that Elliot[15] determined the symmetry of the second conduction band as Γ_2^-, but Gross, analyzing the influence of oriented elastic deformations on excitons of the blue and violet series, showed that the experimental results can be explained only if this band has Γ_{12}^- symmetry.[1]

We now study in greater detail the structure of the 1*s*

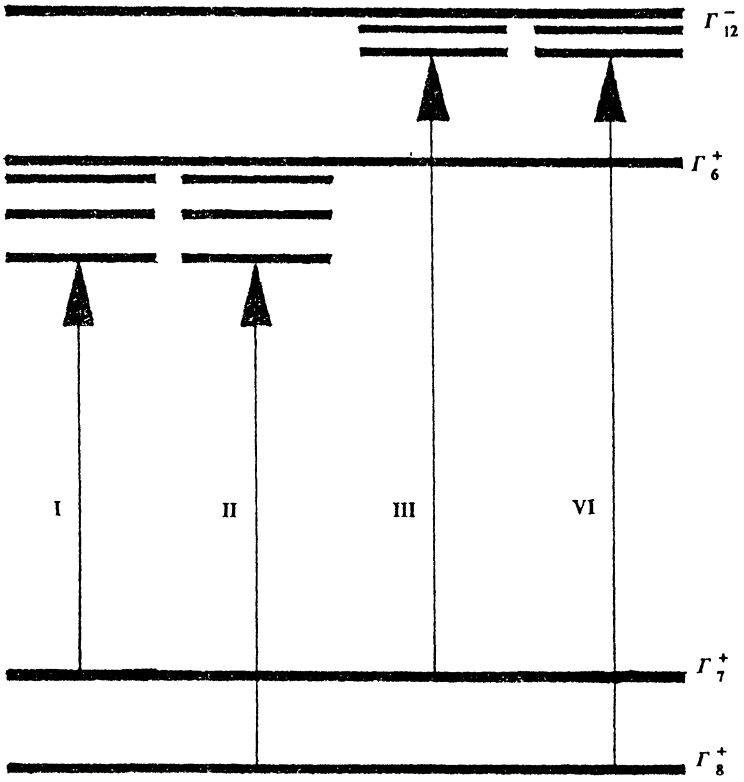

FIG. 2. Band structure of cuprous oxide crystal. I, II, III, and IV are transitions resulting in the appearance of, respectively, yellow, green, blue, and violet exciton series.

exciton of the yellow series. It is well-known that large-radius excitons (Wannier excitons) are related to a definite electron-hole pair, the relative electron-hole motion being described by a hydrogen-like wave function. In this case the number and type of symmetry of the excitonic levels at the center of the Brillouin zone is determined by expanding[17] the direct product $\Gamma_e \times \Gamma_h \times \Gamma_{eh}$ of the irreducible representations of the electron Γ_e, the hole Γ_h, and their relative motion Γ_{eh} in irreducible representations of the double point group O_h', and the irreducible representation of the 1*s* state of the yellow exciton Γ_{ex} can be written in the form

$$\Gamma_{ex} = \Gamma_7^+ \times \Gamma_6^+ \times \Gamma_{eh} = \Gamma_6^+ \times \Gamma_7^+ \times \Gamma_1^+ = \Gamma_2^+ + \Gamma_{25}^+, \tag{3}$$

where the fact that for *s* excitons the irreducible representation Γ_{eh} has Γ_1^+ symmetry has been taken into account.

It follows from Eq. (3) that the 1*s* exciton of the yellow series splits into a nondegenerate paraexciton Γ_2^+ and a triply degenerate orthoexciton Γ_{25}^+. The experimental data show (see, for example, Ref. 18) that the energy level of the paraexciton lies $\Delta E \approx 96\ \mathrm{cm}^{-1}$ below the energy level of the orthoexciton.

Since the valence band Γ_7^+ has the same parity as the conduction band Γ_6^+, electronic transitions into the orthoexcitonic state are allowed only in the quadrupole approximation. Transitions to the paraexcitonic level are forbidden in all orders of perturbation theory. These features of the selection rules explain, in particular, the fact that the absorption at the frequency corresponding to the first line of the yellow excitonic series is weaker than for higher-order lines.[19]

3. SELECTION RULES FOR NONRESONANT HRS

The method of group-theoretical analysis of Raman scattering in crystals, which is based on the relation between the RS tensors and Clebsch–Gordan coefficients of crystalline space groups, was proposed by J. Birman in Refs. 8 and 20. In the present work we applied this method to investigate hyper-Raman scattering, which is a nonlinear optical effect of order higher than RS.

Let an electromagnetic wave, polarized in the plane of the crystallographic axes α and β, propagate in the crystal. In this case the expression for the intensity of light scattered into the solid angle $d\Omega$ and polarized along the γ crystallographic axis has the form

$$I_{\mathrm{HR}} \simeq C \left| \sum_{\alpha\beta\gamma} \beta_{\alpha\beta\gamma} \varepsilon_\alpha^i \varepsilon_\beta^i \varepsilon_\gamma^s \right|^2, \tag{4}$$

where $\beta_{\alpha\beta\gamma}$ is the hyperpolarizability tensor of rank 3, $\varepsilon_\alpha^i(\varepsilon_\beta^i)$ and ε_γ^s are the unit polarization vectors of the exciting and scattered radiations, and the fundamental constants are included in the coefficient. For nonresonant HRS the tensor $\beta_{\alpha\beta\gamma}$ must be symmetric under permutations of all indices, and its dependence on the wave vectors of the exciting and scattered radiations can be neglected, since the scattering process occurs at the center of the Brillouin zone.

For scattering by phonons the hyperpolarizability operator $\hat{\beta}_{\alpha\beta}(\mathbf{R})$ is defined as follows:

$$\beta_{\alpha\beta\gamma} = \int \chi_{n'}(\mathbf{R}) \hat{\beta}_{\alpha\beta\gamma}(\mathbf{R}) \chi_n(\mathbf{R}) d\mathbf{R}, \tag{5}$$

where $\chi_n(\mathbf{R})$ and $\chi_{n'}(\mathbf{R})$ are the wave functions of the initial and final characteristic states of the crystal with vibrational quantum numbers n and n', and $\mathbf{R}$ is the instantaneous position of the nuclei in the crystalline lattice. The operator $\hat{\beta}_{\alpha\beta\gamma}(\mathbf{R})$ can be expanded in a Taylor series in the displacements $\mathbf{u}$ of the nuclei from their equilibrium positions $\mathbf{R}_0$, but it is more convenient to use instead of $\mathbf{u}$ the normal vibrational coordinates Q_σ^j of the lattice, which are described by the σth row of the *j*th irreducible representation:

$$\hat{\beta}_{\alpha\beta\gamma}(\mathbf{R}) = \hat{\beta}_{\alpha\beta\gamma}(\mathbf{R}_0) + \sum_{j\sigma} \hat{\beta}_{\alpha\beta\gamma}(\mathbf{R}_0; j, \sigma) Q_\sigma^j + \dots . \tag{6}$$

The operator $\hat{\beta}_{\alpha\beta\gamma}$ and the normal vibrational coordinates Q_σ^j transform as follows under the action of a symmetry element S of the point group G of the crystal:

$$\hat{\beta}_{\alpha\beta\gamma}(\mathbf{R}) \overset{S}{\rightarrow} \hat{\beta}'_{\alpha\beta\gamma}(\mathbf{R}) = \sum_{\lambda\mu\nu} S_{\alpha\lambda} S_{\beta\mu} S_{\gamma\nu} \hat{\beta}_{\lambda\mu\nu}(S^{-1}\mathbf{R}), \tag{7}$$

$$Q_\sigma^j \overset{S}{\rightarrow} Q_\sigma^{j'} = \sum_\tau D^{(j)}(S)_{\tau\sigma} Q_\tau^j, \tag{8}$$

where $D^{(j)}$ is the matrix of the *j*th irreducible representation of the group G and $\hat{\beta}'_{\alpha\beta\gamma}(\mathbf{R}) = \hat{\beta}'_{\alpha\beta\gamma}(\mathbf{R})$.

An expression for the contribution of the *j*th vibration to the hyperpolarizability tensor can be obtained from Eqs. (5)–(8):

$$\begin{aligned}
\beta_{\alpha\beta\gamma}(j,\sigma) &= \sum_{\lambda\mu\nu} S_{\alpha\lambda} S_{\beta\mu} S_{\gamma\nu} \sum_\tau D^{*(j)}(S)_{\sigma\tau} \beta_{\lambda\mu\nu}(j,\tau) \\
&= \sum_{\lambda\mu\nu} \sum_{ann'} U_{\alpha\beta,an} D^{(a)}(S)_{nn'} U^{-1}_{an',\lambda\mu} S_{\gamma\nu} \sum_\tau D^{*(j)} \\
&\quad \times (S)_{\sigma\tau} \beta_{\lambda\mu\nu}(j,\tau) \\
&= \sum_{\lambda\mu\nu} \sum_{ann'} U_{\alpha\beta,an} U^{-1}_{an',\lambda\mu} \sum_{kmm'} V_{n\gamma,km} \\
&\quad \times V^{-1}_{km',n'\nu} D^{(k)}(S)_{mm'} \sum_\tau D^{*(j)} \\
&\quad \times (S)_{\sigma\tau} \beta_{\lambda\mu\nu}(j,\tau),
\end{aligned} \tag{9}$$

where the unitary matrices U and V reduce the matrix $D^{(v)}_{\alpha\beta,\lambda\mu} = S_{\alpha\lambda} S_{\beta\mu}$ and the product $D^{(a)}_{nn'} \times S_{\gamma\nu}$ to the form

$$D^{(v)}_{\alpha\beta,\lambda\mu}(S) = \sum_{ann'} U_{\alpha\beta,an} D^{(a)}_{nn'}(S) U^{-1}_{an',\lambda\mu} \tag{10}$$

and

$$D^{(a)}_{nn'} \times S_{\gamma\nu} = \sum_{kmm'} V_{n\gamma,km} D^{(k)}_{mm'} V^{-1}_{km',n'\nu}.$$

Summing the expression (9) over all symmetry elements of the group G and using the fact that the irreducible representations are orthogonal,[17] we have

TABLE I. Nonzero components of the hyperpolarizability tensor for nonresonant HRS in cuprous oxide.

		$\varepsilon^s = x$	$\varepsilon^s = y$	$\varepsilon^s = z$
Γ_2^-	σ_1	$\begin{pmatrix} . & . & . \\ . & . & a \\ . & a & . \end{pmatrix}$	$\begin{pmatrix} . & . & a \\ . & . & . \\ a & . & . \end{pmatrix}$	$\begin{pmatrix} . & a & . \\ a & . & . \\ . & . & . \end{pmatrix}$
$\Gamma_{15'}^-$	x	$\begin{pmatrix} b & . & . \\ . & c & . \\ . & . & c \end{pmatrix}$	$\begin{pmatrix} . & c & . \\ c & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & c \\ . & . & . \\ c & . & . \end{pmatrix}$
	y	$\begin{pmatrix} . & c & . \\ c & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} c & . & . \\ . & b & . \\ . & . & c \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & c \\ . & c & . \end{pmatrix}$
	z	$\begin{pmatrix} . & . & c \\ . & . & . \\ c & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & c \\ . & c & . \end{pmatrix}$	$\begin{pmatrix} c & . & . \\ . & c & . \\ . & . & b \end{pmatrix}$
$\Gamma_{25'}^-$	σ_1	$\begin{pmatrix} . & . & . \\ . & d & . \\ . & . & -d \end{pmatrix}$	$\begin{pmatrix} . & d & . \\ d & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & -d \\ . & . & . \\ -d & . & . \end{pmatrix}$
	σ_2	$\begin{pmatrix} . & -d & . \\ -d & . & . \\ . & . & . \end{pmatrix}$	$\begin{pmatrix} -d & . & . \\ . & . & . \\ . & . & d \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & d \\ . & d & . \end{pmatrix}$
	σ_3	$\begin{pmatrix} . & . & d \\ . & . & . \\ d & . & . \end{pmatrix}$	$\begin{pmatrix} . & . & . \\ . & . & -d \\ . & -d & . \end{pmatrix}$	$\begin{pmatrix} d & . & . \\ . & -d & . \\ . & . & . \end{pmatrix}$

$$\beta_{\alpha\beta\gamma}(j,\sigma)=\sum_{\lambda\mu\nu\tau}\sum_{ann'}U_{\alpha\beta,an}U^{-1}_{an',\lambda\mu}V_{n\gamma,j\sigma}\times V^{-1}_{j\tau,n'\nu}\beta_{\lambda\mu\nu}(j,\tau)/l_j, \qquad (11)$$

where l_j is the dimension of the jth irreducible representation. Since the linear combination $\Sigma_{\lambda\nu\tau n'}\times U^{-1}_{an',\lambda\mu}V^{-1}_{j\tau,n'\nu}\beta_{\lambda\mu\nu}(j,\tau)$ depends only on the irreducible representations a and j, the expression (11) can be rewritten in the form

$$\beta_{\alpha\beta\gamma}(j,\sigma)=\sum_{an}U_{\alpha\beta,an}V_{n\gamma,j\sigma}c(j,a), \qquad (12)$$

where $U_{\alpha\beta,an}$ and $V_{n\gamma,j\sigma}$ are Clebsch–Gordan coefficients.

The expression (12) can be used to determine the nonzero components of the hyperpolarizability tensor of any point-symmetry group by simply substituting the corresponding Clebsch–Gordan coefficients.[21] The nonzero components of the hyperpolarizability tensor of a cuprous oxide crystal and their linear combinations, belonging to irreducible representations of the vibrations of the crystalline lattice are given in Tables I and III. Our linear combinations are identical to the results of Ref. 22, where the action of all symmetry elements of this group on the hyperpolarizability tensor was studied in order to obtain the selection rules in each crystallographic point group. We note that in the case of resonance scattering the determination of the selection rules by this method is highly problematical, while with the help of the expression (12) the specific resonance conditions can be easily taken into account and the corresponding HRS tensor can be easily found.

4. SELECTION RULES FOR RESONANT HRS WITH THE PARTICIPATION OF THE 1*s* EXCITON OF THE YELLOW SERIES

In order to take into account resonance effects in the interaction of radiation with matter it is necessary to invoke the microscopic scattering theory. According to this theory the intensity of HRS by optical phonons is determined in the fourth order of perturbation theory (see, for example, Ref. 23):

$$I_{\mathrm{HR}}=I(\omega_L,\omega_S,\omega_0)=C\left|\sum_{abc}\frac{\langle f|\hat{H}_{ER}|c\rangle\langle c|\hat{H}_{ER}|b\rangle\langle b|\hat{H}_{ER}|a\rangle\langle a|\hat{H}_{ER}|i\rangle}{(E_c-\hbar\omega_S)(E_b-2\hbar\omega_L)(E_a-\hbar\omega_L)}\right|^2, \qquad (13)$$

where ω_L, ω_S, and ω_0 are, respectively, the frequencies of the exciting and resonant photons and the phonon frequency; $\hat{H}_{ER}$ and $\hat{H}_{EL}$ are the electron–photon and electron–phonon interaction Hamiltonians; $|i\rangle$ and $|f\rangle$ are the initial and final states; and, $|a\rangle$, $|b\rangle$, and $|c\rangle$ are the virtual intermediate states of the crystal.

Two-photon resonance between the exciting radiation and the 1*s* excitonic level of cuprous oxide occurs when $2\hbar\omega_L\simeq E_{1s}$, where E_{1s} is the energy of the 1*s* state of the exciton of the yellow series. In this case the intermediate states $|b\rangle$ are the real excitonic states $|1s\rangle$ and therefore only the irreducible representations of $D^{(a)}$ which transform in accordance with the irreducible representation Γ_{25}^+ need be included in Eq. (10). In addition, under conditions of resonant scattering the tensor $\beta_{\alpha\beta\gamma}$ exhibits permutation

TABLE II. Linear combinations of the nonzero components of the HRS and RHRS tensors in cuprous oxide which transform according to the irreducible representations of the vibrations of the crystalline lattice.

	HRS	RHRS
Γ_2^-	β_{xyz}	$(\beta_{xyz}+\beta_{yzx}+\beta_{xzy})$
Γ_{12}^-		$(\beta_{yzx}-\beta_{xzy},$ $\{\beta_{yzx}+\beta_{xzy}-2\beta_{xyz}\}/\sqrt{3})$
Γ_{15}^-	$(\beta_{xxx},\beta_{yyy},\beta_{zzz})$ $(\beta_{xyy}+\beta_{xzz},$ $\beta_{xxy}+\beta_{yzz},$ $\beta_{xxz}+\beta_{yyz})$	$(\beta_{xzz}+\beta_{xyy},$ $\beta_{yzz}+\beta_{xyx},$ $\beta_{yzy}+\beta_{xzx})$
Γ_{25}^-	$(\beta_{xyy}-\beta_{xzz},$ $\beta_{yzz}-\beta_{xxy},$ $\beta_{xxz}-\beta_{yyz})$	$(\beta_{xyy}-\beta_{xzz},$ $\beta_{yzz}-\beta_{xyx},$ $\beta_{xzx}-\beta_{yzy})$

symmetry only with respect to the first two indices α and β, associated with the polarization of the exciting radiation. Taking into account these features, the expression (12) under conditions of resonant HRS with the participation of the 1*s* exciton can be represented in the form

$$\beta_{\alpha\beta\gamma}(j,\sigma)=\sum_n U_{\alpha\beta,n}V_{n\gamma,\sigma}c(j)+\sum_n U_{\beta\alpha,n}V_{n\gamma,\sigma}c(j). \tag{14}$$

Using the formula (14) we calculated the nonzero components of the resonant hyperpolarizability tensor and their linear combinations for all characteristic vibrations of the crystalline lattice of cuprous oxide. The computational results are presented in Tables II and III, respectively.

TABLE III. Nonzero components of the hyperpolarizability tensor for resonant HRS in cuprous oxide with participation of the 1*s* exciton of the yellow series.

		$\varepsilon^s=x$	$\varepsilon^s=y$	$\varepsilon^s=z$
Γ_2^-,	σ_1	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&a\\\cdot&a&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&a\\\cdot&\cdot&\cdot\\a&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&a&\cdot\\a&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$
Γ_{12}^-,	σ_1	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&b\\\cdot&b&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&-b\\\cdot&\cdot&\cdot\\-b&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$
	σ_2	$\begin{pmatrix}\cdot&\cdot&b/\sqrt{3}\\\cdot&\cdot&\cdot\\\cdot&b/\sqrt{3}&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&b/\sqrt{3}\\\cdot&\cdot&\cdot\\b/\sqrt{3}&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&-2b/\sqrt{3}&\cdot\\-2b/\sqrt{3}&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$
		$\varepsilon^s=x$	$\varepsilon^s=y$	$\varepsilon^s=z$
Γ_{15}^-,	x	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&c&\cdot\\c&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&c\\\cdot&\cdot&\cdot\\c&\cdot&\cdot\end{pmatrix}$
	y	$\begin{pmatrix}\cdot&c&\cdot\\c&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&c\\\cdot&c&\cdot\end{pmatrix}$
	z	$\begin{pmatrix}\cdot&\cdot&c\\\cdot&\cdot&\cdot\\c&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&c\\\cdot&c&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$
Γ_{25}^-,	σ_1	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&d&\cdot\\d&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&-d\\\cdot&\cdot&\cdot\\-d&\cdot&\cdot\end{pmatrix}$
	σ_2	$\begin{pmatrix}\cdot&-d&\cdot\\-d&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&d\\\cdot&d&\cdot\end{pmatrix}$
	σ_3	$\begin{pmatrix}\cdot&\cdot&d\\\cdot&\cdot&\cdot\\d&\cdot&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&-d\\\cdot&-d&\cdot\end{pmatrix}$	$\begin{pmatrix}\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\\\cdot&\cdot&\cdot\end{pmatrix}$

5. CONCLUSIONS

It is evident from Table II that, in contrast to nonresonant scattering, the diagonal components of the RHRS tensor vanish for all characteristic vibrations of the cuprous oxide crystal. As a result of this, the process of resonant HRS in Cu_2O is determined by the off-diagonal components of the hyperpolarizability tensor, and the scattering intensity should be largest when the exciting radiation is polarized at an angle $\vartheta = \pi/4$ with respect to the crystallographic axes. In addition, under the conditions of RHRS the Γ_{12}^- vibration symmetry, which is forbidden under nonresonant conditions was observed previously only in resonant RS spectra, is allowed in the Cu_2O crystal.[4-6]

Since all *ns* states of the yellow excitonic series ($n = 1,2,3,...$) are described by the same irreducible representations, the selection rules which we derived are applicable for resonant HRS when any *s* exciton of this series participates. Therefore, by tuning the frequency of the probe radiation over the region of excitonic excitations it should be possible to observe in turn the scattering lines corresponding to different *s* states. We note that besides two-photon absorption, resonant HRS is the only method for investigating excitonic excitations of cuprous oxide with $n > 1$, since in the case of resonant RS intense dipole–dipole scattering by *p*-excitonic states is superposed on the quadrupole–dipole scattering when *s* excitons participate.[24] As a result of this superposition, scattering by only the 1*s* exciton of the yellow series—this exciton being removed from the nearest *p*-state by almost 930 cm^{-1}—can be observed in resonant RS. Under the conditions of RHRS, in contrast to RRS, the intensity of scattering with the participation of *s* excitons should be significantly higher than the intensity of scattering by *p* states, since resonant HRS is realized through a two-photon dipole transition, allowed for *s* states but forbidden for *p* states.

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