Second-harmonic generation resonant to the 1S orthoexciton level of cuprous oxide

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The electric-quadrupole second-harmonic (SH) signal resonant to 1S yellow orthoexciton in Cu_2O is observed. SH signals for the polycrystalline and the single crystal have been investigated. The polarization property of the SH signal has also been studied. The enhanced resonant SH signal can be ascribed to the small damping constant of the electric-quadrupole transition of the orthoexciton. The polarization properties of the SH signal are explained in terms of the energy consideration of the nonlinear optical properties of solids proposed by Pershan. In addition, resonant hyper-Raman scattering of the Γ_{12}^- phonon is also observed. [S0163-1829(96)01720-2]

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Because of their importance in fundamental physics, the exciton properties of Cu_2O have been studied extensively for 40 years, since the first measurement of excitons in Cu_2O.[1] These studies include exciton structures,[2] resonant Raman scattering,[3] excitonic Bose-Einstein condensation and excitonic superfluidity,[4–6] and so on. The 1S yellow orthoexciton of Cu_2O interacts with the radiation field through an electric-quadrupole coupling. Since Terhune, Makev, and Savage[7] first observed optical second-harmonic light in a calcite crystal, investigations of electric-quadrupole effects on second-harmonic generation (SHG) have seldom been performed for solids, as far as we know, as the effects are very weak. The electric-quadrupole resonant effect may be obvious because the electric-quadrupole transition causes a narrowing of the spectral line compared to that of a dipole-allowed transition; i.e., the orthoexciton state has a small damping constant. As far as we know, no report has been made about researches on the pure electric-quadrupole effect in resonant SHG in solids. Here we give experimental results of resonant SHG for the 1S yellow orthoexciton of Cu_2O, and briefly discuss the experimental results.

When infrared light excites a Cu_2O sample, we can observe its luminescence, both with SHG and hyper-Raman scattering. The properties of the luminescence depend on some relaxation mechanism. However, those of the SHG and hyper-Raman scattering hardly depend on the relaxation mechanism.[8] Even if the sample does not produce any luminescence, the SHG and hyper-Raman scattering may be very strong. Resonant two-photon absorption may give us a way to obtain a low-temperature exciton system which is favorable to excitonic Bose-Einstein condensation.[4,5] Thus a study of the contribution of resonant SHG and hyper-Raman scattering to the two-photon excitation spectra is of importance.

A tunable infrared laser light was obtained from a Solar CF-151M LiF color center laser pumped by a Spectron SL803 YAG (yttrium aluminum garret) pulse laser light with the repetition rate of 10 Hz and a pulse width of 12 ns. By a lens with 300-mm focal length, an infrared laser beam with 0.2 mJ/pulse and a 1-cm-diameter cross section was focused on sample immersed in superfluid helium. The signal was detected by a Princeton Instruments 576G/RB ICCD through a Solar MDD500×2 spectrometer. In order to study sample dependence and SHG properties, we used two kinds of samples: one was a polycrystalline film prepared in our laboratory by oxidizing a copper film at 99999% purity and with a thickness of 0.1 mm in oxygen at about 60 Torr and at about 1030 °C, and the other a natural Cu_2O single crystal. The orientation of the natural Cu_2O single crystal was identified by the x-ray Laue pattern method. The geometry used during experiment is shown in Fig. 1.

The upper part of Fig. 2 shows the photoluminescence spectrum of the homemade sample at 2 K excited by 5145-Å light from a cw Ar^+ laser. A luminescence line at 6096 Å is due to radiative annihilation of a triply degenerate Γ_{25}^+ orthoexciton,[9] and a line at 6136 Å is due to Γ_{12}^- phonon-assisted recombination of the orthoexciton. The lower part of Fig. 2 shows emission spectra under the excitation of infrared lights with wavelengths between 12 185 and 12 195 Å. These spectra are independent of the measurement direction shown in Fig. 1(a). The peak photon energy of the emission line around 6096 Å is exactly twice as large as the exciting photon energy. The orthoexciton luminescence can also exist in this region. The Γ_{12}^- phonon-assisted orthoexciton luminescence is, however, very weak, and the orthoexciton luminescence peak should be independent of the excitation photon energy. Thus the luminescence contribution to the peak intensity at about 6096 Å can be neglected. These facts suggest that these emissions at about 6096 Å are SH light. Strictly speaking, in these signals hyper-Rayleigh scattering may be contained because hyper-Raman scattering is observed, as seen below. The signal was very strong, capable of being seen by eye. The emission intensity drastically increases by two times as the exciting light energy coincides with the orthoexciton energy. When half the wavelength of the pump laser was out of this region we were not able to detect any signal, even by using a long-time integration with

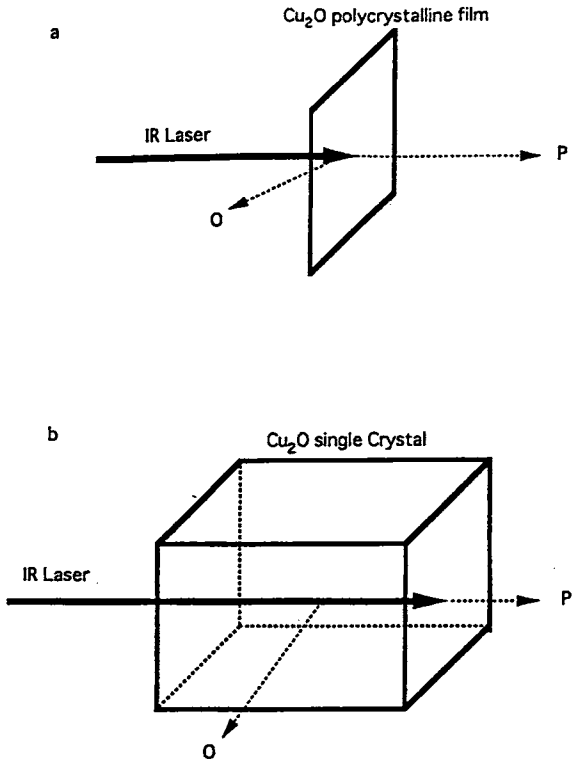

FIG. 1. The geometry used during the experiment. Signals are measured along the laser direction **P** or in the direction **O** which is perpendicular to the laser direction, or forms some other angles with the laser direction. (a) The case of the polycrystalline film Cu_2O. (b) The case of the single crystal, where the IR laser direction is along the [1,1,1] direction with a polarization along [1,−1,0].

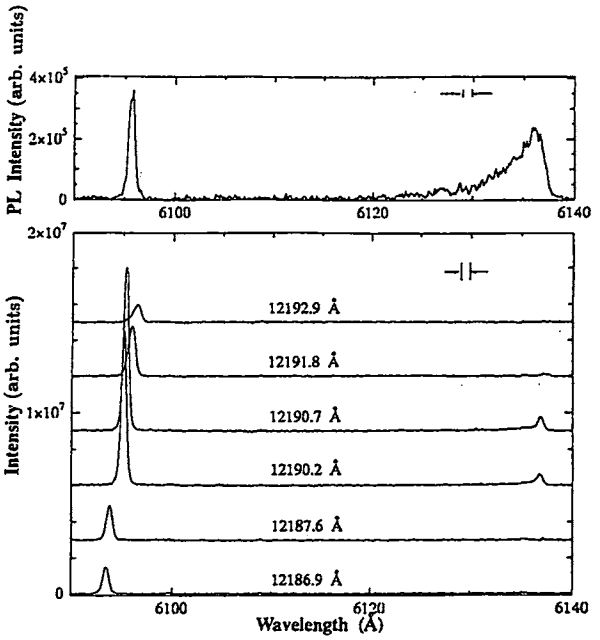

FIG. 2. The top spectrum is the photoluminescence spectrum of the polycrystalline sample excited by 5145 Å at 2 K. The lower part shows emission spectra in the excitation of IR light with different wavelengths at 2 K. The excitation wavelengths are shown in the figure.

our system. Considering that the intensity of the nonresonant SHG is smaller than the level of the noise, the enhancement of the resonant SHG is estimated to be more than 10^6. This means that the energy of the second-harmonic light resonates to the orthoexciton level. Figure 3 is the same as Fig. 2, but the scale of the intensity is changed. The structures at about 6136.5 Å are composed of one sharp peak labeled by an arrow, and a small broad one. The former shifts along with the pump laser, and the latter almost does not change, as labeled by a vertical dotted line. We assign the former to hyper-Raman scattering of the Γ_{12}^- phonon, and the latter to the luminescence of the Γ_{12}^- phonon-assisted orthoexciton. The results for a large single crystal show that this SHG does not result from surface effects.

The strong light of the resonant second harmonic means that the nonlinear susceptibility is large. Here we take the resonance for $1S$ yellow orthoexciton and multipole effect into account, and neglect the nonresonant terms, because we cannot observe a nonresonant signal. We can express the effective second-harmonic susceptibility χ as[10]

$$\chi \propto \sum_I \frac{\langle g|e^{-i\mathbf{k}_s\cdot\mathbf{r}}\mathbf{e}_s\cdot\mathbf{p}|\text{ortho}\rangle\langle\text{ortho}|e^{i\mathbf{k}_I\cdot\mathbf{r}}\mathbf{e}_i\cdot\mathbf{p}|I\rangle\langle I|e^{i\mathbf{k}_I\cdot\mathbf{r}}\mathbf{e}_i\cdot\mathbf{p}|g\rangle}{(E_{\text{ortho}}-2\hbar\omega+i\Gamma)(E_I-\hbar\omega)}, \tag{1}$$

where **e** is unit polarization vector of light, **p** is a momentum operator, **k** is a wave vector, Γ is a damping constant of the orthoexciton, $\hbar\omega$ is an incident photon energy, $|g\rangle$, $|I\rangle$, and $|\text{ortho}\rangle$ are wave functions of the ground state, the Ith intermediate state, and the orthoexciton state, respectively, and E_{ortho} and E_I are energies of the orthoexciton and the Ith intermediate state, respectively. Subscripts i and s refer to the pump laser light and SH light, respectively. Because of the symmetry effect, in the dipole approximation, the matrix element $\langle g|\mathbf{e}\cdot\mathbf{p}|\text{ortho}\rangle$ is zero, and, hence, we have to consider the higher-order term, i.e., the electric-quadrupole effect: $\langle g|(i\mathbf{k}_S\cdot\mathbf{r})(\mathbf{e}\cdot\mathbf{p})|\text{ortho}\rangle$, which is generally much weaker than the dipole effect. The area of the orthoexciton absorption band is three orders of magnitude weaker than that of the $2P$ exciton band,[11] and thus the matrix element for the transition to the orthoexciton state is smaller by several tens than that to the $2P$ exciton state. However, it should be noticed that a striking enhancement of χ may be expected by

the very small factor $E_{ortho}-2\hbar\omega+i\Gamma$ in the denominator of Eq. (1). This factor can become as small as ~0.1 meV.[3] Compared with the nonresonant case, i.e., $E_{ortho}-2\hbar\omega\sim 1$ eV, a ten-thousandfold enhancement in χ can be expected. Because the relevant matrix element of the excitons of Cu_2O is very small, as we know, a nonresonant SH signal has not been observed. Resonant enhancement makes an observation of the SH signal possible. A measurement of the absolute values of the nonlinear susceptibilities is underway.

In order to investigate the polarization properties of second-harmonic generation, we measured the signal from a single crystal. The plane index of a natural Cu_2O single crystal is (1,1,1). When the infrared laser light travels along the [1,1,1] direction with polarization [1,−1,0], a very strong and highly oriented light is observed along [1,1,1] direction. This SHG light has a long coherent length which makes the SHG grow strong.[10] Compared with SH light, the hyper-Raman scattering light accompanied by the Γ_{12}^- phonon emission is too weak to be seen in the spectrum of the same scale of intensity as in Fig. 2. In Fig. 4 are shown spectra (broken lines) of this SH light intensity, as well as absorption (a solid line) and photoluminescence (a dotted line) spectra at 2 K. Open circles and crosses represent SH light intensities when the electric-field vectors are perpendicular and parallel to the electric-field vector of the IR laser light, respectively. The results show that SH light appears in strong resonance with the orthoexciton level between 6095 and 6097 Å, and outside of this region we cannot obtain any signal. At the peak position, SH light whose polarization is perpendicular to the polarization of the excitation light is much stronger than that of the parallel polarization.

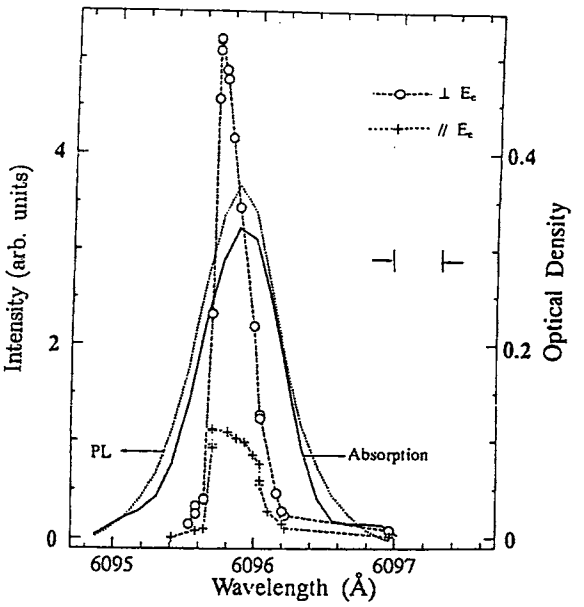

FIG. 4. The wavelength dependences of the second-harmonic light intensity are shown by circles and crosses corresponding to polarizations $E_s\perp E_e$ and $E_s\|E_e$, respectively. Here E_s and E_e are electric-field vectors of the SH light and the exciting IR light, respectively. The absorption and photoluminescence spectra of the $1S$ orthoexciton are also shown with solid and dotted lines, respectively. The photoluminescence is measured in the excitation of 5145-Å light.

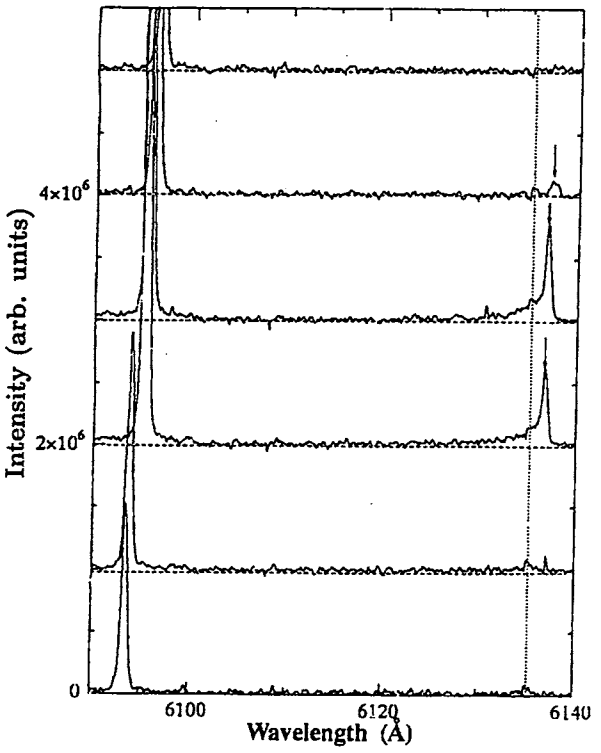

FIG. 3. The hyper-Raman scattering of Γ_{12}^- phonons (labeled by arrows), and the Γ_{12}^- phonon-assisted luminescence (labeled by the vertical dotted line) of the polycrystalline sample under excitation by lights with different wavelengths.

The above polarization results may be understood from an energy consideration of the nonlinear optical properties of solids proposed by Pershan.[12] In an energy consideration for electric-quadrupole effects on SHG, Pershan obtained an equation for the nonlinear current source density $J_i^{NLS}(2\omega)$:

$$J_i^{NLS}(2\omega)=2i\omega\sum_{ljk}\nabla_k\chi_{jlki}E_j(\omega)E_l(\omega), \qquad (2)$$

where χ is the nonlinear susceptibility, and E the excitation electric field (for detailed definition see Ref. 12). We assume that the excitation light is a plane wave. For an isotropic material, it is easy to demonstrate that for a plane wave at frequency ω moving with the wave vector such that $\mathbf{k}(\omega)\cdot\mathbf{E}(\omega)=0$, the nonlinear current given by Eq. (2) is parallel to $\mathbf{k}(\omega)$. Hence we cannot obtain the SHG in an isotropic material.[12] Let us consider the situation for the isotropic material again in a right-handed coordinate system as shown in Fig. 5(a). The polarization of the excitation $\mathbf{E}(\omega)$ is along the [1,−1,0] direction, and the wave vector of the excitation light beam is along the [1,1,1] direction. Using the tensor of χ,[12] we obtain that the current components in the x, y, and z directions, J_x, J_y, and J_z, are the same in magnitude and sign, so that the total current is along [1,1,1], that is, the direction of $\mathbf{k}(\omega)$ [see Fig. 4(a)]. Similarly, for Cu_2O with a cubic structure, we obtain that J_x and J_y are the same in magnitude and sign, but their magnitude is different from J_z.

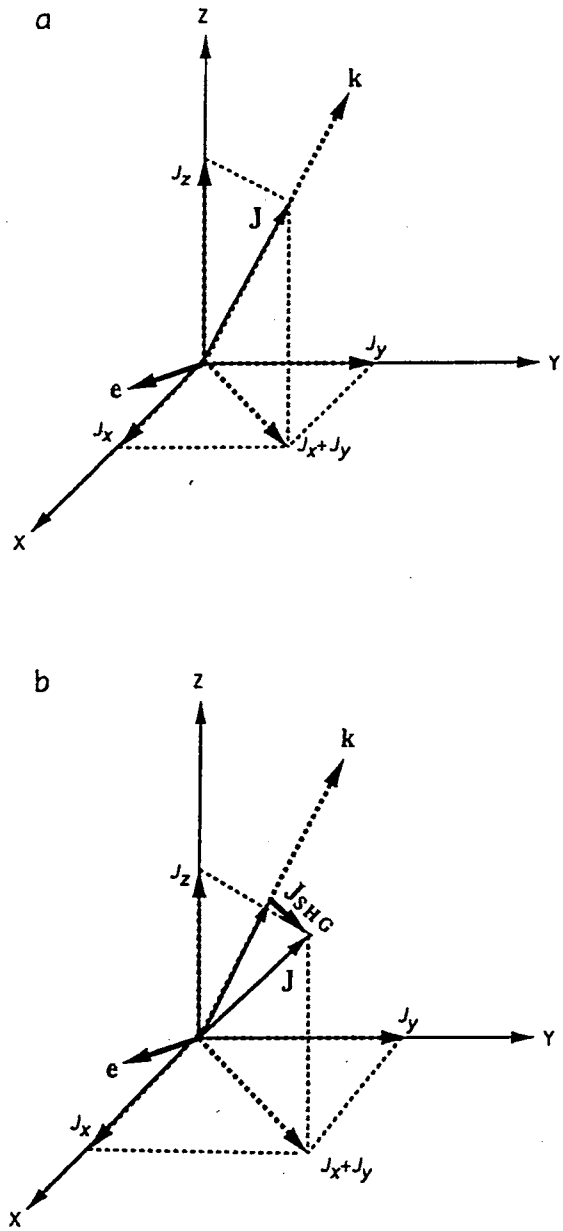

FIG. 5. The nonlinear current source density for isotropic material and that for cubic Cu_2O are shown in (a) and (b), respectively. The unit polarization vector of excitation light along the [1,−1,0] direction is represented by e, and the wave vector of the excitation light along the [1,1,1] direction by k.

This results in a component perpendicular to the [1,1,1] direction, as well as one along the [1,1,1] direction [see Fig. 5(b)]. The component J_{SHG} perpendicular to [1,1,1] contributes to SHG. J_{SHG} is also perpendicular to [1,−1,0], the polarization direction of the excitation light. Therefore in the ideal case that the excitation light is a plane wave and the material has no absorption (the Pershan assumption), we can only observe SH light with a polarization perpendicular to the polarization direction of the excitation light [1,−1,0]. However, weak SH light with polarization along [1,−1,0] was also observed in the present experiment. This means that the real case is different from the ideal case. This might originate from the fact that the excitation light is not an exact plane wave, and that the crystal also has a slight absorption due to the $1S$ orthoexciton.

SH signals with a small coherent length were also measured in the direction perpendicular to the direction of the excitation light [see Fig. 1(b)]. The line shape in exciting light of different wavelengths is similar to that of the polycrystallines, as shown in Figs. 2 and 3. This means that the coherent length of the SH light in the polycrystalline sample is small. The results also show that the observed SHG does not result from surface effects.

The luminescence is dependent on some relaxation mechanism, but the SHG and the hyper-Raman scattering do not depend very much on the relaxation mechanism.[8] The SHG and hyper-Raman scattering can be very strong even though the sample does not give any luminescence. Our homemade polycrystalline films, which give no luminescence, as shown on the top of Fig. 2, can also give the same SHG intensity as shown in the lower part of Fig. 2. When the natural single crystal is resonantly excited to the orthoexciton level by the two-photon absorption of the infrared laser light, a very strong and broad luminescence band appears between 6140 and 6500 Å. The luminescence band contains many sharp peaks that do not shift with the excitation light wavelength. The structures of the luminescence band are the same as those in the excitation of 5145-Å light. These are the luminescences associated with the impurities or defects in the Cu_2O single crystal. The integrated strength of the broad-band is more than ten orders of magnitude stronger than that of the $1S$ orthoexciton luminescence with the Γ_{12}^- phonon. The photogenerated orthoexcitons may relax not only to the $1S$ paraexciton but also to the defect and impurity states. In the pure crystal, Bose-Einstein condensation of the $1S$ orthoexciton may be easily realized[4] because the exciton density may be large enough and the exciton temperature as low as the bath temperature 2 K, which is much lower than that in the one-photon excitation[4,5] in which excitons with a large kinetic energy are generated and relaxed to the $1S$ orthoexciton by emitting many phonons.

In summary, we have given experimental data for resonant electric-quadrupole SHG in Cu_2O polycrystallines and single crystals. SHG with a long coherent length is obtained in the single crystal, and the property of polarization is measured. The observed strong light due to resonant SHG can be understood microscopically. That is, the small damping constant of the orthoexciton $\Gamma \sim 0.1$ meV may result in a ten-thousandfold enhancement of the nonlinear susceptibility χ. The polarization properties of the SH light are explained in terms of the macroscopic energy consideration of the nonlinear optical properties of solids, as proposed by Pershan. We have also observed resonant hyper-Raman scattering by the Γ_{12}^- phonon.

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