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Effects of Rayleigh scattering on photovoltaic spectra associated with 1*s* orthoexcitons in Cu_2O

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Photovoltaic (PV) spectra in the 1*s* orthoexciton region of Cu_2O natural single crystals have been measured as a function of the location of the illumination spot in the temperature range between 28 and 185 K. The spectral shape analysis of the exciton-mediated PV reveals the effective contribution of Rayleigh scattering light in the sample, as confirmed by off-axis transmission measurements.

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Photoelectric spectra near the band-edge region of Cu_2O have strong correlation with absorption spectra associated with excitons.[1] Tselepis *et al.* have given a model to explain the exciton-mediated photovoltaic (PV) generation in Cu_2O (Ref. 2) as an extension of a standard model used in the theory of solar cells.[3] In their model, photogenerated excitons diffuse into a thin layer where they are ionized completely by the built-in electric field in the proximity of the electrodes to give PV signals. Fortin *et al.* used this effect to detect the ballistic propagation of excitons in high-density photoexcitation.[4] We have been interested in the origin of the large prompt signal followed by a delayed one due to the arrival of the excitonic packet at the electrodes.

On the other hand, we have reported[5,6] that the PV signal is generated under illumination at locations distant from electrodes, even when the distance is much larger than the relevant diffusion lengths of excitons and free carriers. This led us to consider the possibility of some light scattering processes occurring within the crystal. In fact, elastic scattering light is usually observed under the one-photon resonance excitation around the 1*s* orthoexciton region even if the optical quality of the sample seems to be satisfactory as far as the excitonic absorption,[7] luminescence,[8] and cyclotron resonance[9] spectra are concerned. In the present work we studied PV spectra as a function of the temperature of the lattice and the distance of the illumination spot from the edge of electrodes in order to examine the effect of light scattering on the PV spectral shape.

A single crystal of Cu_2O $[2\,\mathrm{mm}\,(H)\times 6\,\mathrm{mm}\,(W)\times 1\,\mathrm{mm}\,(D)]$, cut from a natural cuprite, was used as a sample. The crystal looks very transparent and shows strong intrinsic emission of excitonic origin at low temperature. To measure the PV signals, electrodes were attached to mechanically polished and chemically etched surfaces facing each other. The magnitude of the signal depends on the material of the electrodes. However, the spectral shape is similar and its sign is the same at 145 K for three different combinations of the electrodes: Cu-carbon (Electrodag 112, Acheson), Au-Au, and carbon-carbon. We used Au-Au electrodes because of its moderate (about the half of that of Cu-carbon electrodes) sensitivity and good linearity against the incident laser power. The light source was a conventional dye-laser (Rhodamine B in methanol) pumped by a nitrogen laser of ~5 nsec duration. The spectral width of the dye laser light was $\leqslant 0.3$ meV. The photon energy of the incident light was calibrated by atomic lines of a Ne lamp. The PV spectra did not depend on the pulse energy in the range between 0.6 and 5 μJ/pulse.

The sample was sandwiched with cold fingers of a cryostat with a couple of mica sheets for electric insulation. A boxcar integrator was used to average PV signals by setting the sampling gate for 2 μs at the maximum of the signal pulse. The duration of the signal pulse was mainly determined by the electric properties of the circuit, including the internal resistance of the sample. Transmission spectra of the sample were measured by a conventional monochromator with a stabilized Xe lamp as the light source.

The temperature of the sample was determined consistently from the temperature dependence of the resonance energy of the 1*s* orthoexcitons and the intensity of the phonon-assisted indirect absorption. The resonance energies that have been reported by one-photon[10] and two-photon[11] spectroscopy were used to obtain the empirical Varshi's equation in units of eV: $E(T)=2.033-(3.8\times 10^{-4}T^2)/(145+T)$, where T is the lattice temperature in K. The absorption coefficients at respective photon energies are consistent with the value determined rigorously by O'Hara *et al.*[12]

Solid curves in Fig. 1 show the PV spectra at various temperatures with $x=0.3$ mm, where x is the location of the excitation spot P of diameter ~ 0.16 mm, measured from the edge of an electrode on the front surface marked by A in the inset (a). The PV spectra are shown after being corrected by the spectral gain distribution of the incident laser light. Continuous structure due to one longitudinal-optical (1LO) (Γ_3^-) phonon-assisted transition is clearly seen with the sharp resonance due to the 1*s* orthoexcitons. With the increase of the temperature, the shape of the PV spectra changes in a complex manner.

We tried to apply Tselepis's model to reproduce the PV spectra observed. The PV signal J is given by

$$J \propto [\exp(\alpha w)-1]\exp(-\alpha t)+\frac{\alpha L}{\alpha^2L^2-1}\left((\alpha L-1)\times\exp\{-[\alpha(t-w)]\}+\frac{\exp[-(t-w)(\alpha-1/L)]-\alpha L}{\cosh[(t-w)/L]}\right), \tag{1}$$

with the absorption coefficient α and three length parameters: the thickness of the sample t, the diffusion length of

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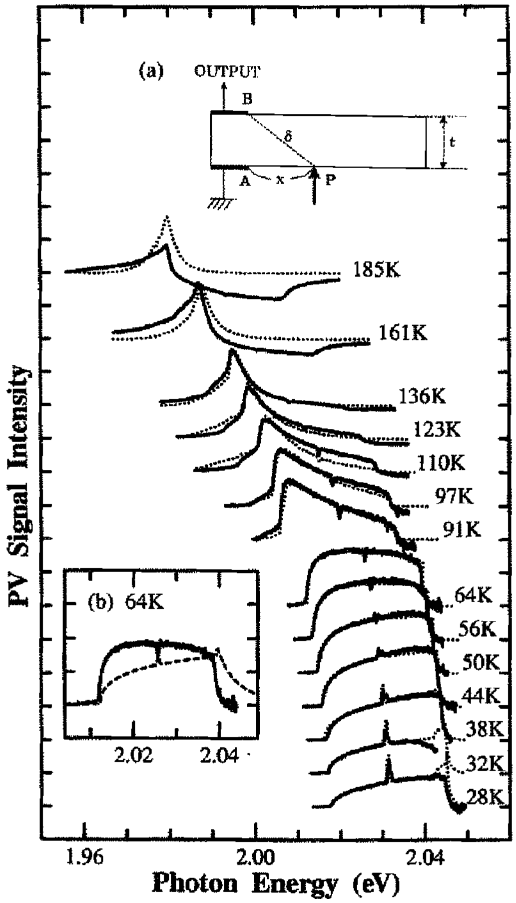

FIG. 1. Temperature dependence of PV spectra with $x = 0.3$ mm. Inset (a) shows the configuration of the electrodes (A,B) and the excitation spot (P). Solid curves are PV spectra observed. Dotted and dashed curves represent the spectra calculated with $\alpha = 3\alpha_{\text{abs}}$ and $\alpha = \alpha_{\text{abs}}$, respectively.

the excitons L, and the thickness of the exciton-ionization region w. In our calculation we tentatively used the distance δ between P and the edge of the rear electrode B instead of t. The first term of Eq. (1) stands for the direct creation of the carriers in the ionization region while the second term comes from the solution to a continuous equation of excitons with diffusive motion. The first term has a spectral dependence similar to the second one in a limit of our case, $w \ll L \ll \delta$.

The dashed curve in the inset (b) of Fig. 1 represents a PV spectrum calculated from the absorption spectrum measured at 64 K, taking reliable length parameters referring to the temperature dependence of the diffusion length of the excitons.[13] The calculated spectrum, however, does not reproduce the experimental data shown by the solid curve in the inset. It was found that the PV spectrum is well reproduced if the measured absorption coefficient α_{abs} is multiplied by about 3 at respective photon energies. A similar tendency was seen at other temperatures. Dotted curves in Fig. 1 represent the calculated spectra taking $\alpha = 3\alpha_{\text{abs}}$, $\delta = 1.04$ mm, $L = 50$ μm, and $w = 100$ nm.

Solid curves in Fig. 2 represent similar PV spectra obtained with $x = 2$ mm as a function of the detuning from the resonance energy of the 1s orthoexcitons. We found again that the absorption coefficient has to be multiplied by about 3 to reproduce the PV spectra, as shown by dotted curves.

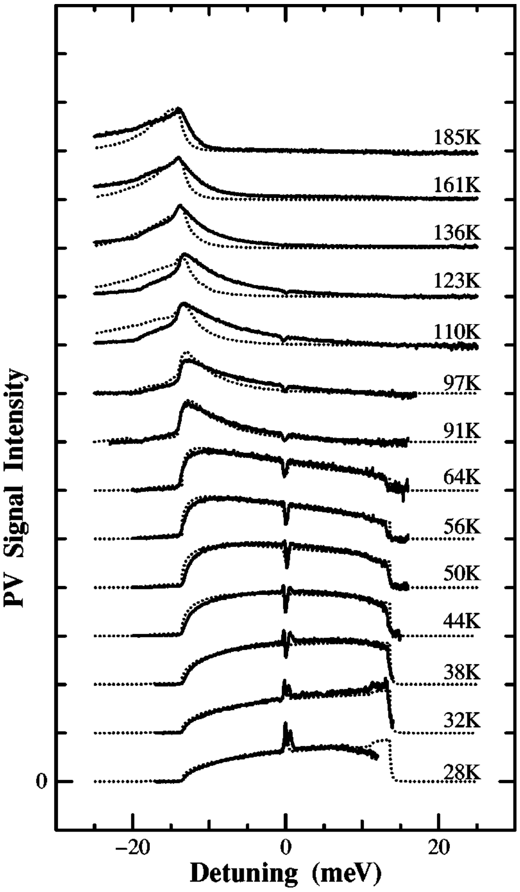

FIG. 2. Solid curves are PV spectra obtained with $x = 2$ mm at various temperatures. Dotted curves are calculated taking $\alpha = 3\alpha_{\text{abs}}$.

To understand these facts, we measured absorption spectra for a similar sample under the configuration shown in the inset of Fig. 3. The location of the illuminated spot and the window of the masks are also marked as P and B for the convenience of comparison with the inset (a) of Fig. 1. The solid curve in Fig. 3 is an example of absorption spectra obtained by on-axis geometry at 77 K. The intensity of the transmitted light I is well described by the usual Lambert's law, $I = I_0 \exp(-\alpha_{\text{abs}} t)$, where I_0 and α_{abs} are the intensity of the transmitted light in the transparent region and the absorption coefficient, respectively. The dotted curve is a similar spectrum obtained by off-axis geometry with $x \sim 0$ mm at the same temperature. In this case, it was found that the signal intensity is well reproduced by an equation of $I = I_0'$ $\exp(-3\alpha_{\text{abs}}\delta)$, where δ is the direct distance from P to B. The intensity of the signal in the transparent region I_0' was measured as $\sim 10^{-4} I_0$. The factor of 3 was almost independent of the photon energy and x. The situation did not change at various temperatures.

According to theoretical and experimental analyses[16] based on the integrodifferential equation given by Chandrasekhar,[17] the extinction coefficient of light in a medium where scattering significantly occurs is expressed by

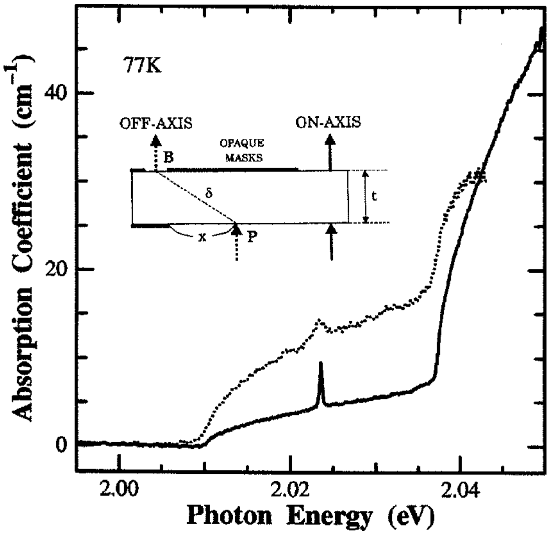

FIG. 3. Absorption spectra at 77 K in on-axis (solid curve) and off-axis (dotted curve) geometry. In off-axis geometry, the band pass of the monochromator is widened so as to detect the weak signals with a sufficient signal-to-noise ratio.

the sum of $\alpha_{\rm abs}$ and $\alpha_{\rm scatt}$, where $\alpha_{\rm scatt}$ is the measure of the scattering. This concept has been discussed in astrophysics[18] and medical photobiology.[19] We consider that the light in the crystal may be strongly influenced by the multiscattering.

The origin of the scattering to give I_0' may be due to the dynamical fluctuation[14] of the lattice or static density fluctuation[15] in the crystal. In both cases dipole-allowed states of large oscillator strength predominantly take part in the elastic scattering. In the present experiment, the origin would be the latter. The scattering on the front surface may also contribute to I_0'.

If we assume that the intensity of the transmitted light can be expressed as $I=I'_{0\rm abs}+\alpha_{\rm scatt})\delta]$, $\alpha_{\rm scatt}$ should have the same spectral dependence as $\alpha_{\rm abs}$ in the energy range of the relevant indirect absorption continuum. The spectral character can be explained by resonance Rayleigh scattering mediated by the $1s$ orthoexcitons with the assistance of LO (Γ_3^-) phonons. This process is regarded as a coherent coupling of a dipole-allowed phonon-assisted transition and the reverse one. The selection rule is identical to the 2LO resonance Raman process.[20] The efficiency of the scattering should be proportional to $\alpha_{\rm abs}(\omega_i)$ (Ref. 21) where ω_i is the photon energy of the incident and scattering light, giving the same spectral dependence of $\alpha_{\rm scatt}$ and $\alpha_{\rm abs}$. On the other hand, the reabsorption of the anti-Stokes 2LO (Γ_3^-) Raman scattering light does not contribute to the present phenomenon because the spectral shape of $\alpha_{\rm scatt}\propto\alpha_{\rm abs}(\omega_s)$ is different from that of $\alpha_{\rm abs}(\omega_i)$, where $\omega_s=\omega_i+2\omega_{LO}$ is the photon energy of the Raman scattering light, with ω_{LO} being the energy involving phonons.

In the high-temperature range, the PV signal of the opposite sign appears at the high-energy side when $x=0.3$ mm. According to Eq. (1) with $w\ll L\ll t$, the PV signal saturates when the absorption coefficient exceeds $1/t$ where t is the distance of the light passing through the crystal to arrive at the electrode. For the front electrode, $t\sim x$ is very small and the signal is expected to be maximized at the higher-energy side than that from the rear electrode. Therefore, we consider that the ''negative'' PV signal originates from the front electrode. This is also supported by the fact that the signal rapidly decreases as x increases (see Fig. 2). At low temperatures, absorption is small in the $1s$ exciton region so that no negative signal manifests itself due to the cancellation by the large positive signal from the rear electrode, maximized at $\alpha\sim1/\delta$. The study on the PV spectra in the lower temperature range is also in progress, where the diffusion length of the excitons should become longer to give some effects on the PV spectrum.

In conclusion, we have measured the PV spectra mediated by $1s$ orthoexcitons in a natural crystal of $\mathrm{Cu_2O}$ as a function of temperature and the location of the illumination spot against the electrodes. The effect of Rayleigh scattering was observed thanks to the high sensitive character of the PV generation in the crystal.

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[1] E.F. Gross and B.V. Novikov, J. Phys. Chem. Solids **22**, 87 (1961); E.F. Gross and I. Pastrnyak, Fiz. Tverd. Tela (Leningrad) **1**, 837 (1959) [Sov. Phys. Solid State **1**, 758 (1959)]; **1**, 162 (1959) [**1**, 143 (1959)].

[2] E. Tselepis, E. Fortin, and A. Mysyrowicz, Phys. Rev. Lett. **59**, 2107 (1987).

[3] S. M. Sze, *Physics of Semiconductors Devices*, 2nd ed. (Wiley, New York, 1981).

[4] E. Fortin, S. Fafard, and A. Mysyrowicz, Phys. Rev. Lett. **70**, 3951 (1993).

[5] N. Nagasawa, N. Naka, and M. Hasuo, Fiz. Tverd. Tela (St. Petersburg) **40**, 921 (1998) [Phys. Solid State **40**, 847 (1998)].

[6] N. Nagasawa and N. Naka, in Meeting Abstracts of 1998 Asian Pacific Forum on Science and Technology, p. 84 (1998).

[7] H. Matsumoto, K. Saito, M. Hasuo, S. Kono, and N. Nagasawa, Solid State Commun. **97**, 125 (1996).

[8] Y. Petroff, P.Y. Yu, and Y.R. Shen, Phys. Rev. B **12**, 2488 (1975).

[9] T. Ohyama, T. Ogawa, and H. Nakata, Phys. Rev. B **56**, 3871 (1997).

[10] E.F. Gross, Nuovo Cimento Suppl. **3**, 672 (1956); J.B. Grun, M. Sieskind, and S. Nikitine, J. Phys. Chem. Solids **19**, 189 (1960); I.S. Gorban' and V.B. Timofeev, Fiz. Tverd. Tela (Leningrad) **3**, 3584 (1961) [Sov. Phys. Solid State **3**, 2606 (1962)]; A. Mysy-

rowicz, D. Hullin, and A. Antonetti, Phys. Rev. Lett. **43**, 1123 (1979); **43**, 1275(E) (1979); D. Snoke, J.P. Wolfe, and A. Mysyrowicz, *ibid.* **59**, 827 (1987).

[11] M. Hasuo (unpublished).

[12] K.E. O'Hara, J.R. Gullingsrud, and J.P. Wolfe, Phys. Rev. B **60**, 10 872 (1999).

[13] D.P. Trauernicht and J.P. Wolfe, Phys. Rev. B **33**, 8506 (1986).

[14] V. L. Ginzburg, A. A. Sobyanin, and A. P. Levanyuk, in *Light Scattering Near Phase Transitons*, edited by H. Z. Cummins and A. P. Levanyuk (North-Holland, Amsterdam, 1983), p. 3.

[15] A. P. Levanyuk, A. S. Sigov, and A. A. Sobyanin, in *Light Scattering Near Phase Transitons*, Ref. 18, p. 129.

[16] R.A. Groenhuis, H.A. Ferwerda, and J.J. Ten Bosch, Appl. Opt. **22**, 2456 (1983); **22**, 2463 (1983).

[17] S. Chandrasekhar, *Radiative Transfer* (Oxford University Press, New York, 1960).

[18] L.G. Henyey and J.L. Greenstein, Astrophys. J. **93**, 70 (1941).

[19] M. Ochsner, J. Photochem. Photobiol., B **32**, 3 (1996).

[20] P.Y. Yu and Y.R. Shen, Phys. Rev. B **12**, 1377 (1975).

[21] S. Permogorov, in *Modern Problems in Condensed Matter Sciences*, edited by V. M. Agranovich and A. A. Maradudin (North-Holland, Amsterdam, 1979), Vol. 2; P. Y. Yu and M. Cardona, in *Fundamentals of Semiconductors* (Springer, Heidelberg, 1995).