Strain confinement and thermodynamics of free excitons in a direct-gap semiconductor

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Long-lived paraexcitons have been confined by a strain-induced parabolic potential well in Cu_2O. The excitons are found to behave as a highly diffusive classical gas at the crystal lattice temperature, as determined from their spatial and energy distributions between 1.5 and 4.2 K. Strain confinement and spatially selective resonant excitation provide a new method for examining the thermodynamics and interparticle kinetics of this direct-gap exciton.

It has been demonstrated that strain confinement is a versatile method for controlling a gas of excitonic particles.[1] By applying an appropriate inhomogeneous stress, photoexcited particles are confined to a parabolic potential well located inside the bulk crystal. The excitons occupy a specific volume in which excitonic thermodynamics can be studied away from any perturbing surface. Until now this method has been successful only in high-purity germanium and silicon, where the indirect band gap inhibits rapid electron-hole recombination. In direct-gap semiconductors, rapid radiative recombination normally limits excitonic lifetime to $\lesssim 10^{-8}$ sec, precluding the attainment of thermal equilibrium at the lattice temperature.

In this paper we report the first strain-confinement of direct-gap excitons—in Cu_2O. Excitons in this semiconductor are of the Wannier-Mott type which exhibit hydrogen-like series and have been the object of many high-resolution spectroscopic experiments.[2] They are characterized by a small Bohr radius (~ 10 Å) and large binding energy (~ 150 meV). Both ortho- and paraexcitons are predicted to exist, but radiative recombination of the (Γ_2^+) para state is highly forbidden by parity and band symmetry. However, phonon-assisted recombination of paraexcitons has been recently observed in high-purity natural-growth Cu_2O, and exceptionally long lifetimes, up to 13 μsec, were reported.[3] It is this long-lived paraexciton which is the object of our study.

The experiments were performed on a high-purity, natural-growth crystal cut and polished to a cube of lateral dimension 1.7 mm. Stress was applied uniaxially in the [001] direction by a spherical glass stresser with radius of curvature $R \simeq 1.6$ cm, as shown in the inset of Fig. 1. With the Hertzian geometry, a point of highest stress is created inside the crystal a few hundred micrometers below the contact. As we have recently shown,[4] strain lowers the exciton energy, implying that the aforementioned stress maximum corresponds to an energy minimum. Excitons are created directly in the well by tuning a cw dye laser to the locally downshifted low-energy edge of the phonon-assisted orthoexciton. Paraexcitons are efficiently generated by down-conversion of these short-lived orthoexcitons. Luminescence emitted from the potential well was viewed along a <110> axis and the direct (no phonon) paraexciton emission was analyzed both as a function of energy and space.

The spatial distribution of excitons confined in the strain well is shown in Fig. 1(a) for three lattice temperatures. These distributions were independent of the laser power for incident powers $\lesssim 1$ mW. The data were obtained by scanning the crystal image across the small entrance slit of a spectrometer, giving a spatial resolution of about 50 μm. To detect all paraexcitons within the slit width it is essential to adjust the spectral resolution to encompass all energies occupied in the energy gradient. This is accomplished by providing a large exit slit to the spectrometer.

The measured spatial distributions are explained very well

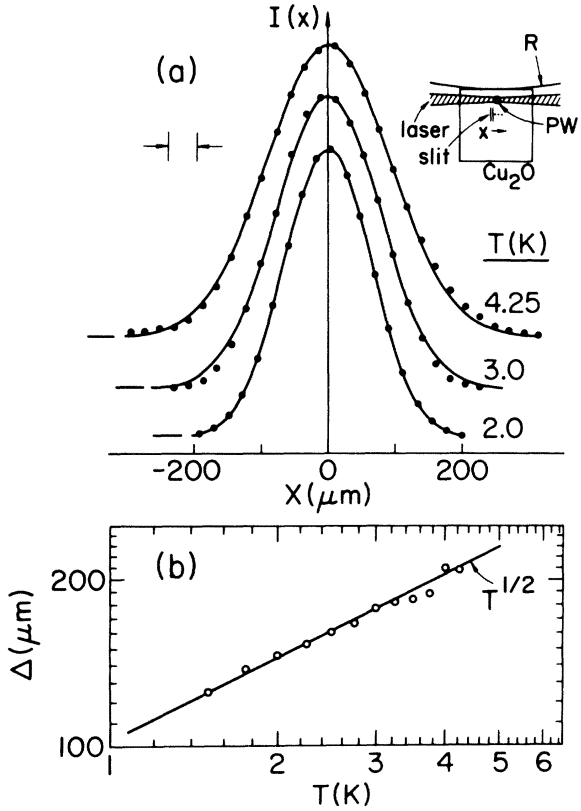

FIG. 1. (a) Spatial profiles of the luminescence from paraexcitons confined in a potential well (PW). The graphs are shifted vertically for display purposes. Zero intensity is indicated to the left of each curve. Dots are experimental points, and solid lines are Eq. (1), with T equal to the lattice temperature. (b) Log-log plot of the temperature variation of the full width at half maximum Δ. Open circles are experimental points and the solid line indicates the predicted $T^{1/2}$ behavior. $\lambda_{laser} \approx 608$ nm.

by assuming that the paraexcitons are in thermal equilibrium with the lattice in a parabolic potential, $V=\alpha r^2$. The chemical potential of these particles is constant across the well; that is,

$$kT\ln n(r)=kT\ln n(0)-\alpha r^2 \ ,$$

where $n(r)$ is the local density at a distance r from the center of the well, leading directly to the distribution

$$n(r)=n(0)\exp(-\alpha r^2/kT) \ . \qquad (1)$$

The solid curves in Fig. 1 represent this Gaussian function for a single well parameter $\alpha=23$ meV/mm^2. The full width at half maximum (Δ) of this distribution is $(2.77kT/\alpha)^{1/2}$, independent of particle mass or density. In Fig. 1(b) we show that this prediction is valid over the temperature range 1.5 to 4.2 K. The paraexcitons in Cu_2O behave as an ideal classical gas with temperature equal to the lattice temperature under low-power excitation.

An important implication of these results is that the paraexcitons in high-purity Cu_2O must have a very high diffusivity, since they fill a volume having a 100-μm radius within their lifetime τ. In terms of a diffusion constant D, this means that the excitonic diffusion length is greater than the well size, i.e., $\sqrt{D\tau}>100$ μm. With a typical lifetime $\tau\approx 300$ ns (see below), we deduce $D>300$ cm^2/sec. This large D and long τ suggest the feasibility of macroscopic exciton transport measurements in Cu_2O, as previously demonstrated in Si and Ge.[5]

Let us now consider the spectral shape of the luminescence of excitons in the parabolic well. The equilibrium energy distribution of particles has the form

$$N(\epsilon)=D(\epsilon)f(\epsilon) \ , \qquad (2)$$

where $\epsilon=0$ corresponds to zero kinetic energy of the particles. For particles in a parabolic potential, the density of states $D(\epsilon)$ is proportional to ϵ^2 instead of $\epsilon^{1/2}$ for a free gas.[1] The distribution function is

$$f(\epsilon)=(e^{(\epsilon-\mu)/kT}-1)^{-1}\approx e^{(\mu-\epsilon)/kT}$$

for low density.

To compare with this simple predicted energy distribution, it is necessary to collect the luminescence with high spectral resolution while spatially integrating over the entire potential well. This is accomplished by summing spectra taken at successive slit positions across the well (see inset of Fig. 1), or by simply collecting the luminescence scattered from a crystal surface. The spatially integrated spectra for three lattice temperatures are shown in Fig. 2(a). The shapes of these spectra are in reasonable agreement with the theoretical curves [solid lines and Eq. (2)], and the T dependence of the full widths increases approximately as predicted [Fig. 2(b)]. The theoretical curves are Eq. (2) convolved with the measured resolution function of our spectrometer with T taken as the lattice temperature. The only fitting parameter is the overall intensity.

The luminescence spectra shown in Fig. 2(a) correspond to the *no-phonon* recombination of paraexcitons. These spectra are quite different from the no-phonon spectra for an unstressed or homogeneously stressed system. For example, the no-phonon orthoexciton luminescence line in unstressed Cu_2O is extremely sharp. (The no-phonon paraexciton emission should also be extremely sharp but is unobservable in an unstressed crystal.) Therefore the potential well has a profound, predictable effect on the energy distribution of an exciton gas and its luminescence spectrum.

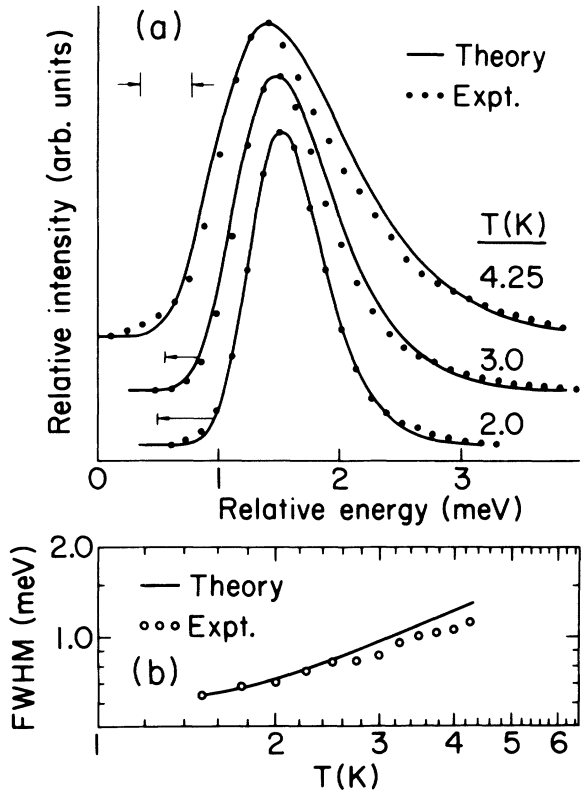

FIG. 2. (a) Spatially integrated line shapes of the paraexciton luminescence. The two lower graphs are shifted horizontally for display purposes, by an amount indicated by the arrows to the left. Theoretical curves are obtained from Eq. (2) convolved with the measured slit function, and T is taken as the lattice temperature. Peak of the line is at approximately 615 nm. (b) Log-log plot of the temperature variation of the spectral full width at half maxium (FWHM). Circles are data and the solid line is the theoretical prediction for a classical gas at the lattice temperature (with no fit parameters).

Finally, we wish to point out that this confinement method may provide a useful means for producing calibrated, high densities of excitons at the lattice temperatures. In contrast with the usual case of surface excitation, it is possible to make an absolute calibration of the excitonic density in the potential well. This involves (1) a determination of the exciton generation rate G by measuring the change in transmitted laser energy through the well region when the stress is removed (i.e., no absorption), and (2) a measurement of the excitonic decay time τ. The average density is simply $G\tau/V$, where V is the known gas volume extracted from Fig. 1. Similar to earlier reports, we found τ to be density dependent. A typical paraexciton lifetime in the strain well at $T=2$ K was 300 nsec, as determined from the instantaneous luminescence decay rate.

For milliwatt-to-watt incident powers, we measured densities in the range $n_{av}=10^{14}$ to 5×10^{15} cm^{-3}, as shown in Fig. 3. (The data shown in Figs. 1 and 2 were taken at an in-

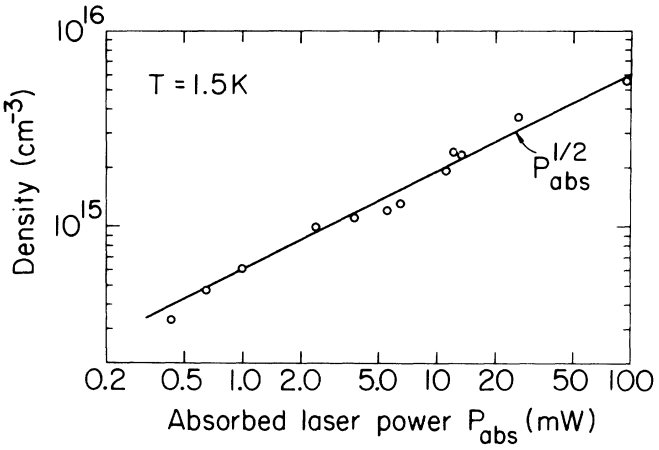

FIG. 3. Paraexciton density vs absorbed laser power, showing the $P^{1/2}$ behavior indicative of an Auger recombination process. Density calibration is explained in the text.

cident power of 0.5 mW.) The dependence of n_{av} on absorbed power is seen to be sublinear and approximated by $P_{abs}^{1/2}$, the solid line in Fig. 3. Similar behavior has been previously reported in unstressed Cu_2O and was attributed to an Auger-like nonradiative decay channel.[6] (The square-root power dependence follows from $dn/dt = -An^2 + G = 0$.) The strain-well method would seem to be well suited for exploring the interparticle kinetics in Cu_2O. Both recombination and interparticle conversion rates have been the subjects of recent experiments and speculation.[6,7]

To summarize, the paraexcitons in Cu_2O display the long lifetimes and large diffusion lengths necessary to achieve thermal equilibrium with the crystal lattice over macroscopic distances. With the strain gradient method it becomes possible to characterize the thermodynamics, transport, and interparticle kinetics of free excitons in this direct-gap material.

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