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Highly Mobile Paraexcitons in Cuprous Oxide

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Using time-resolved luminescence imaging, the authors have measured extremely large mobilities ($\mu \sim 10^7$ cm^2/V-s) and diffusion constants ($D \sim 10^3$ cm^2/s) of paraexcitons in Cu_2O at liquid-helium temperatures. Both μ and D depend strongly on temperature, indicating that phonons are the dominant scattering mechanism, even down to 1.2 K. Clues to the origin of this remarkably weak exciton-phonon scattering are provided by an unusual temperature dependence and a marked stress dependence of the mobility.

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One of the fundamental interactions in a crystalline solid is that between electrons and phonons. This interaction determines the transport properties of electrons in pure semiconductors and metals. A commonly accepted theoretical approach to electron-phonon scattering in a semiconductor was introduced in 1950 by Bardeen and Shockley[1] and is known as deformation-potential scattering. The basic idea is that the scattering time of an electron traveling through the vibrating lattice is related to the static "deformation potential" of the conduction band—i.e., the energy shift of the conduction band with applied stress. This approach has been quite successful in predicting the magnitude and temperature dependence of carrier mobilities in many crystals. Mobility [$\mu =$ (drift velocity)/(electric field)] is the experimental parameter which depends directly on scattering time τ_s as $\mu = e\tau_s/m$, with m the particle mass.

An interesting new test of deformation-potential theory is provided by the exciton, or bound electron-hole pair, which is created by photoexcitation of a semiconductor. A basic question is whether the interaction between electron and hole affects the scattering of phonons from this composite particle. Recent experiments[2] on high-purity Si have indicated that deformation-potential theory applies in a straightforward way to excitons: The mobilities of excitons in Si have reasonably well predicted magnitudes and display the classical $T^{-3/2}$ dependence over a wide temperature range. At the lowest temperature ($T = 1.3$ K), the excitons are extremely mobile, with $\mu \simeq 2 \times 10^6$ cm^2/V-s.

In this Letter, we present evidence for an excitonic particle with much higher mobilities than predicted by standard deformation-potential analysis. Paraexcitons in Cu_2O are shown to exhibit surprisingly high mobilities and diffusion constants, and it is further found that the temperature dependence and magnitude of these experimental parameters can be changed by stressing the crystal. As a graphic illustration of the extreme diffusivity of these excitons, we show in Fig. 1 two time-resolved images of exciton luminescence following a short laser pulse absorbed at the crystal surface. The expansion of the cross-sectional area of the exciton cloud corresponds to a diffusion constant of 600 cm^2/sec at 2 K.

Let us point out some of the special features of excitons in cuprous oxide. They are classic Wannier excitons with a much studied hydrogenlike Rydberg series.[3] The Bohr radius is about 10 Å and the binding energy is about 140 meV. Although the band gap is direct, recombination is parity forbidden since the valence band is d like and the band is s like. While synthetically grown crystals generally have excitonic lifetimes of nanoseconds, it was recently confirmed[4] that excitonic lifetimes in high-purity (naturally grown) samples can exceed 10 μsec, in agreement with the forbidden character of the direct recombination. Analogous to hydrogen, both orthoexcitons and paraexcitons have been observed[5]; they are separated by a 12-meV splitting, with the paraexciton lying lowest in energy. The orthoexciton is quadrupole active, thus displaying stronger absorption and luminescence than the paraexciton, whose highly forbidden recombination is made possible only with the simultaneous emission of an optical phonon.

A quantitative measurement of the paraexciton

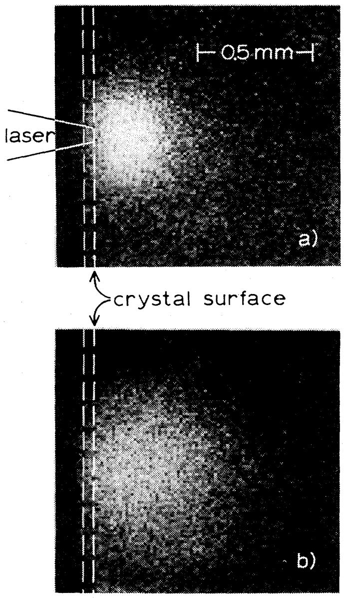

FIG. 1. Time-resolved images of the paraexciton luminescence in Cu_2O at $T = 2$ K, obtained by *x-y* scanning of the crystal image across an entrance aperture of a spectrometer and photon counting. (a) $t = 0.2$ μs after a 100-ns Ar^+ laser pulse is absorbed at the crystal surface (dashed lines). The spacing between dashed lines represents the spatial resolution. (b) $t = 0.6$ μs.

diffusion constant is shown in Fig. 2. A small sample was cut from the same natural crystal which previously displayed long paraexciton lifetimes. By adjusting the wavelength of a dye laser, we could make the optical absorption length approximately equal to the sample length and hence create a fine vertical line of excitons *inside* the crystal, as illustrated in the inset of Fig. 2(a). The phonon-assisted orthoexciton absorption edge was pumped. The orthoexcitons rapidly converted down to paraexcitons.[6] Paraexcitons are detected by their phonon-assisted recombination luminescence.

With ideal pulsed excitation (a δ function at $x = 0$, $t = 0$), the expansion of excitons perpendicular to the excitation line should be given by

$$n(x,t) \propto (4\pi D t)^{-1/2} \exp(-x^2/4Dt) \times \exp(-t/\tau_l),$$

where $n(x,t)$ is the exciton density and τ_l is the exciton lifetime. This is a spreading Gaussian distribution in time whose full width at half maximum $\Delta(t)$ is given by $\Delta^2(t) = 2.77(4Dt)$. Expansion of the paraexciton cloud at 2 K is shown in Fig. 2(a). All the spatial profiles are normalized to the same peak intensity. Figure 2(b) shows that Δ^2 increases linearly with time, demonstrating the diffusive transport process.

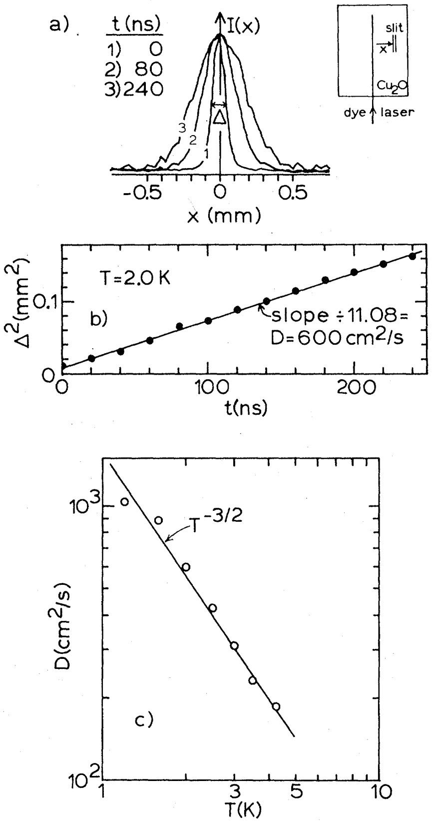

FIG. 2. (a) Expansion of the paraexciton distribution after a 15-ns laser pulse. The time-resolved luminescence profiles are obtained by the scanning of a crystal image across the entrance slit of a spectrometer. (b) Square of the full width at half maximum, Δ, as a function of time. (c) Temperature dependence of the paraexciton diffusion constant. It differs from the $D = (\mu/e) k_B T \sim T^{-1/2}$ expected from standard deformation-potential theory.

The temperature dependence of the measured diffusion constant is given in Fig. 2(c). The observed $T^{-3/2}$ dependence is quite rapid, implying that phonons, not impurities, are the dominant scattering mechanism. A value of approximately 1000 cm^2/s was obtained at $T = 1.2$ K. Assuming that the Einstein relation, $D = (\mu/e)kT$, holds, we find a mobility of approximately 10^7 cm^2/V-s at 1.2 K. Using the recently measured[7] 1*s* exciton mass of $3m_0$, we derive a mean scattering time $\tau_s = \mu m/e = 17$ ns and a mean scattering length $l = 70$ μm. These are exceptionally large values in view of the fact that even for excitons in ultrapure Si, $\tau_s \simeq 1.5$ ns at 1.3 K, corresponding to $l \simeq 15$ μm.

Are the mobilities actually as high as these measured diffusion constants imply? In fact, the temperature dependence of D is more rapid than $T^{-1/2}$ predicted by classical deformation-potential theory.[1] To measure the mobility directly, we applied an inhomogeneous stress to the sample by pressing a rounded plunger against the top of the sample.[2] The band gap narrows with stress, and the curves sketched inside the sample in Fig. 3(a) are approximate contours of constant band-gap energy.

Figure 3(b) shows the drift of paraexcitons in a strain gradient. They were initially created at the crystal surface by a pulsed Ar^+ laser [configuration I in Fig. 3(a)]. The measured drift velocity divided by the spectral energy shift (in electronvolts) per unit distance gives the mobility. At the lowest temperature, 1.5 K, the mobility exceeds 10^7 $\mathrm{cm}^2/\mathrm{V\text{-}s}$. In addition, the $T^{-5/2}$ temperature dependence of μ is consistent with the $T^{-3/2}$ dependence of D, and the Einstein relation. The absolute values of μ are about a factor of 2 higher than those predicted by $\mu_E = eD/k_\mathrm{B}T$. However, uncertainty in the absolute strain-gradient force (error bar) and corrections due to the stress dependence of the paraexciton radiative efficiency could lead to a comparable systematic shift of these data.

The principal question at this point is what is the source of discrepancy between the measured D and μ values and standard deformation-potential theory? We suggest that the answer to this problem is related to the unusual stress dependence of the paraexciton energy[8] in $\mathrm{Cu_2O}$ which is shown in Fig. 3(d). Below about 1 kbar, there is a near-zero slope to the E vs σ curve, suggesting a very small effective deformation potential, $\mathscr{D} \sim dE/d\epsilon$, with ϵ the crystal strain. Indeed, a modified T dependence may result from this situation.[9] If, for example, the initial behavior is quadratic, $E = E_0 - C\epsilon^2$, this implies $\mathscr{D} \sim \epsilon$. For thermal phonons, the strain associated with a given mode varies as $\epsilon^2 \sim k_\mathrm{B}T$, implying $\tau_s^{-1} \sim |\mathscr{D}|^2 T^{3/2} \sim T^{5/2}$, a possible explanation for the observed T dependence.

This hypothesis and Fig. 3(d) imply that the

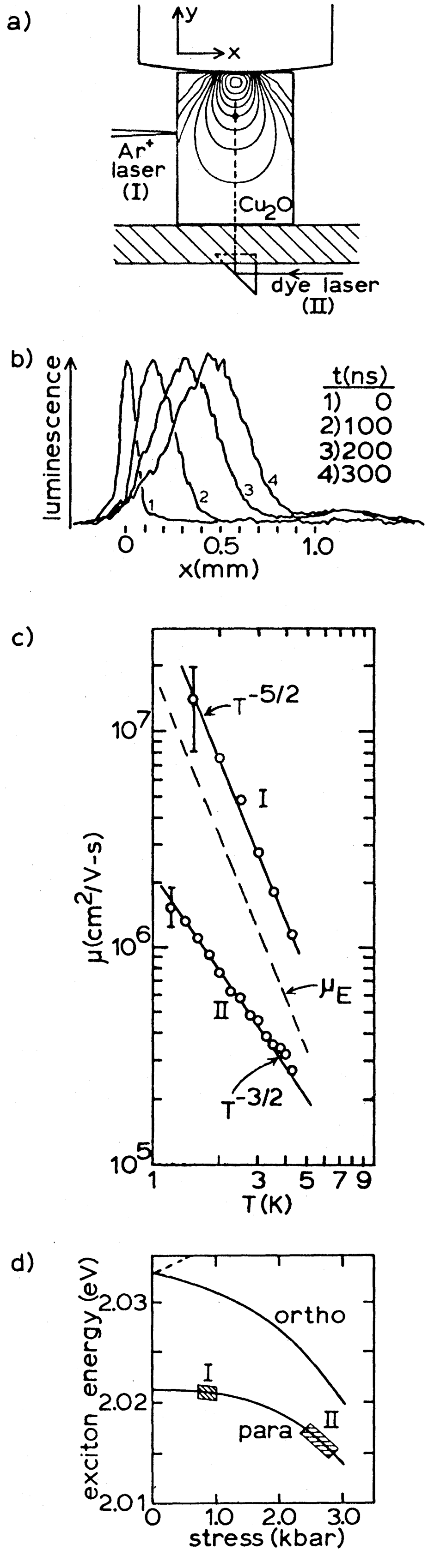

FIG. 3. (a) Strain-gradient configurations for measuring paraexciton drift mobilities in $\mathrm{Cu_2O}$. Configuration I involves surface pumping and low absolute stresses, and configuration II involves spatially selective volume pumping of the higher-stress region. (b) Spatial profiles for configuration I at 1.5 K. The average strain-gradient force was 0.01 eV/cm. (c) Temperature dependences of mobility [$= e \times$ (drift velocity)/force] for low- (I) and high- (II) stress regions. The dashed curve is the zero-stress mobility derived from Fig. 2(c). (d) Stress dependence of the orthoexciton and paraexciton energy.

exciton-phonon interaction should be stress dependent. To test this we devised a different experimental configuration [labeled II in Fig. 3(a)], which initially produces the excitons in a higher-stress region. (Simply applying higher pressure was not possible without breaking the sample.) By tuning the laser wavelength, we resonantly created orthoexcitons at a particular spot in the crystal, and the drift of the thermalized paraexcitons after the 15-ns laser pulse was observed. The resulting mobilities, plotted as the curve labeled II in Fig. 3(c), are indeed much lower than in the low-stress experiment, and the observed $T^{-3/2}$ dependence agrees with standard deformation-potential theory.

In conclusion, we have discovered unexpectedly large mobilities and diffusion constants for paraexcitons in Cu_2O. These are the first measurements of excitonic drift mobilities in a direct-gap semiconductor. The impurity scattering is remarkably small (unmeasurable) for this tiny (10 Å) exciton in our natural crystal. In contrast to usual deformation-potential theory, D and μ are stress dependent and show an unusual temperature dependence at low or zero applied stress. We believe that the cause of these effects lies in the nonlinear variation of paraexciton energy with stress, which is related to the exchange interaction within the exciton.

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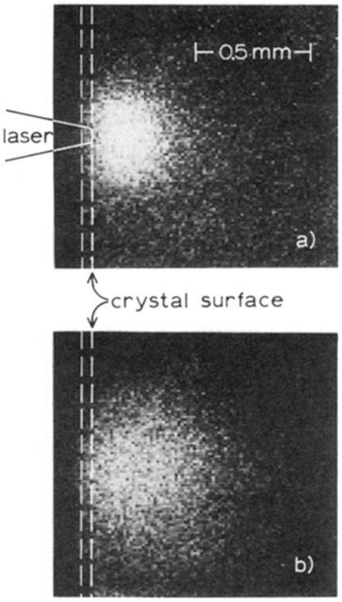

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