LETTER

Giant Rydberg excitons in the copper oxide Cu2O
T. Kazimierczuk, D. Fröhlich, S. Scheel, H. Stolz & M. Bayer

A highly excited atom having an electron that has moved into a level with large principal quantum number is a hydrogen-like object, termed a Rydberg atom. The giant size of Rydberg atoms leads to huge interaction effects. Monitoring these interactions has provided insights into atomic and molecular physics on the single-quantum level. Excitons—the fundamental optical excitations in semiconductors, consisting of an electron and a positively charged hole—are the condensed-matter analogues of hydrogen. Highly excited excitons with extensions similar to those of Rydberg atoms are of interest because they can be placed and moved in a crystal with high precision using microscopic energy potential landscapes. The interaction of such Rydberg excitons may allow the formation of ordered exciton phases or the sensing of elementary excitations in their surroundings on a quantum level. Here we demonstrate the existence of Rydberg excitons in the copper oxide Cu2O, with principal quantum numbers as large as n = 25. These states have giant wavefunction extensions (that is, the average distance between the electron and the hole) of more than two micrometres, compared to about a nanometre for the ground state. The strong dipole–dipole interaction between such excitons is indicated by a blockade effect in which the presence of one exciton prevents the excitation of another in its vicinity.

The Coulomb attraction between a negatively charged electron in the conduction band and a positively charged hole in the valence band leads to the formation of bound exciton states, which are essential to the optical properties of semiconductors. The exciton in bulk crystals has strong similarities with the hydrogen atom, which have been substantiated by the observation of exciton states with binding energies —Ry/√n below the bandgap. Here Ry is the Rydberg energy and n is an integer that is analogous to the principal quantum number n of hydrogen. The observation of highly excited excitons is typically prevented by a small Rydberg energy of a few millielectronvolts (for example, 4.2 meV in the prototypical semiconductor GaAs with n = 3 as its highest observed state), which is about three orders of magnitude smaller than in hydrogen owing to the small reduced mass of the electron and hole and dielectric screening from the many-body surroundings. Therefore, higher exciton states are energetically spaced too closely to each other and to the ionization continuum to be resolvable.

In our search for highly excited excitons we have chosen the semiconductor copper oxide (Cu2O), in which excitons were first observed, facilitated by the comparatively large Rydberg energy of around 100 meV. Cu2O has a direct bandgap (see Supplementary Information). The highest valence and the lowest conduction bands are formed from Cu states, the 3d and 4s orbitals, respectively. The excitons associated with these two bands form the so-called yellow series with energies around 2.1 eV, corresponding to a wavelength of 590 nm for excitation by light. Both bands have the same parity, and therefore electric dipole transitions for excitons with S-type envelope wavefunctions are forbidden. In contrast, excitons with a P-envelope are dipole-allowed, as outlined in the Supplementary Information. In early works, the P-exciton series could be followed up to n = 9 and over the years has been extended to n = 12. Going beyond these n numbers would allow us to create the solid-state analogue to Rydberg atoms. Rydberg atoms have been intensively studied recently because of their attractive properties—long lifetimes, strong dipolar interactions, and so on—which might pave the way for quantum information technologies. Very recently, coupling of the electron in a Rydberg atom (with n = 202 and radius of 2 μm) to a Bose–Einstein condensate was studied.

We studied the exciton spectrum in Cu2O using high-resolution spectroscopy in which the photon energy of a laser with 5–neV linewidth (corresponding to about 1.2 MHz) was scanned across the energy range of interest and the transmitted laser intensity was measured (see Supplementary Information). Usually, the success of semiconductors is based on extremely high crystal quality achieved by artificial fabrication. Oddly, Cu2O artificial crystals are inferior in quality compared to natural crystals. We used a Cu2O crystal with a thickness of 34 μm, cut and polished from a rock mined at the Tsumeb mine in Namibia. The sample was held at a temperature of 1.2 K (see Fig. 1b and c).

In the top panel of Fig. 1a we present the absorption spectrum of P-excitons (that is, an exciton with a P envelope) obtained from the transmission experiments, revealing a large number of lines. To take a closer look at the high-energy part, we zoom into the spectrum with increasing resolution (see the lower panels of Fig. 1a). The exciton lines are labelled by the corresponding principal quantum numbers. Surprisingly, we can uniquely identify states with n up to 25, much higher than previously reported for a solid state system. Such a high n caused us to investigate the extension of the exciton wavefunction. Using the hydrogen relation, the average radius 〈rₙ〉 of an orbital with principal quantum number n and angular momentum l is given by 〈rₙ〉 = aₒₐₚ(3n²−l(l+1)), where aₒₐₚ is the Bohr radius and l = 1 for P-states. The Bohr radius for P-excitons is aₒₐₚ = 1.11 nm (ref. 9). For n = 25 we thus get 〈rₙ〉 ≈ 1.04 μm, corresponding to a huge exciton extension of more than 2 μm, about ten times the light wavelength (see Fig. 1d).

The absorption lines exhibit an asymmetry with a steeper slope on the high-energy flank. The asymmetry is due to interference of a discrete excitonic state and a continuum of states from interaction with optical phonons. From the corresponding fits to each line, the exciton resonance energies Eᵣ can be accurately determined. These energies, shown in Fig. 2a as functions of n, follow the Rydberg formula Eᵣ = EₘᵣORY – 2n²/aₒₐₚ to a good approximation, shown by the fit in Fig. 2a. From the fit we obtain the bandgap energy Eₘᵣ = 2.17208 eV and the Rydberg energy Ry = 92 meV. However, our high-resolution spectroscopy reveals a slight deviation from the Rydberg series, which can be incorporated by employing the concept of quantum defects (see Supplementary Information) such that Eᵣ = EₘᵣORY/(n−δᵣ)² with the P-exciton quantum defect δᵣ = 0.23.

The linewidths Γᵣ shown in Fig. 2b, decrease with increasing n down to a few micro-electronvolts. For principal quantum numbers below n = 10, the lineshapes can be well described by Lorentzians, suggesting homogeneous broadening. Here, the data are in accordance with an inverse cubic law of n. For higher n, the line shape becomes increasingly Gaussian; see Fig. 1a. This indicates that the homogeneous broadening is superimposed by crystal inhomogeneities that are captured by the extended exciton wavefunctions. Yet the linewidth decreases with principal quantum number so that for n = 24 it is as small as 3 μeV. The
energies, which we access by studying the transmission as a function of laser power. The area of each absorption peak corresponds to the absorption strength and is determined by the exciton oscillator strength. The peak areas are shown in Fig. 2c as a function of $n$ for a laser power of $P_L = 20 \, \mu W$, corresponding to an intensity of $6 \, \mu W \, mm^{-2}$. We find that the peak area scales as $1/n^3$, but only in the range up to $n = 17$. This dependence confirms the theoretical analysis for isolated P excitons \cite{3,4}, from which one expects a behaviour proportional to $n^{-5}/n^3 \approx 1/n^3$ for large $n$. However, there are pronounced deviations for $n > 18$ at the excitation power we used; the peak areas are reduced by almost an order of magnitude compared to the expected values.

To explore the origin of this reduction in more detail, we measured the peak area as a function of excitation intensity. Figure 3a shows corresponding absorption spectra from $n = 12$ upwards. With increasing power, the absorption lines continuously decrease, with the higher-lying ones fading away first. The peak areas are plotted as a function of excitation intensity in Fig. 3b, showing a drop starting from a characteristic power level for each principal quantum number. The powers, at which the drop starts, shift to lower excitation intensity with increasing $n$. These results suggest that interaction effects between excitons from which samples of different size and crystal orientation were cut. A large crystal and a thin crystal mounted strain-free in a brass holder. The corresponding light wavelength is shown as the period of the sine function. The bar corresponds to the extension of 1,000 lattice constants.

**Figure 1** | High-resolution absorption spectra of yellow P excitons in Cu$_2$O. a. Spectra are measured with a single-frequency laser on a natural sample of thickness 34 nm at 1.2 K. Peaks correspond to resonances with different principal quantum number $n$. The panels below show close-ups of the areas marked by rectangles in each panel above. b. Photograph of the natural Cu$_2$O crystal. c. Spectra are measured with a single-frequency laser on a natural sample of thickness 34 nm at 1.2 K. Peaks correspond to resonances with different principal quantum numbers we obtained nanosecond lifetimes. d. Wavefunction of the P exciton with $n = 25$. To visualize the giant extension, the corresponding light wavelength is shown as the period of the sine function. The bar corresponds to the extension of 1,000 lattice constants.

**Figure 2** | Dependences of experimentally determined parameters of P-exciton lines on principal quantum number $n$, revealing power-law behaviour. a. Exciton binding energy: square symbols are the resonance energies $E_n$, the solid line represents the $n^{-2}$ dependence expected from the Rydberg formula with $R_Y = 92 \, meV$, and bandgap energy $E_g = 2.17208 \, eV$. Uncertainty of fitting of the exciton energy is negligible in the scale of the plot, as shown by small vertical error bars. b. Square symbols are the experimental absorption linewidth data (defined as FWHM, full width at half maximum) and the solid line shows the $n^{-3}$ dependence. c. Square symbols give experimental oscillator strength (peak area) data in arbitrary units and the solid line shows the $n^{-3}$ dependence expected for a single non-interacting exciton.
are responsible for the reduction of absorption and the increase of transmission. For larger exciton sizes, the interaction effects begin at smaller exciton densities.

To explain the reduction, we propose a dipole blockade effect similar to the one observed for Rydberg atoms. The blockade arises from the dipole–dipole interactions between Rydberg excitons, depending strongly on their separation. If an exciton is created, the energy for exciting another exciton nearby is shifted by the dipole interaction energy, away from the narrow undisturbed absorption line. Thereby a dipole blockade is established: Resonant absorption and exciton creation are no longer possible inside the blockade volume $V_{\text{blockade}}$ in which the dipole interaction energy is larger than the absorption line width $\Gamma_n$.

As a consequence, the absorption $\alpha$ at a given exciton density $\rho_n$ in the illuminated crystal volume is reduced by a factor $(1 - \rho_n V_{\text{blockade}})$ compared to the absorption $\alpha_0(h\omega)$ of the unexcited crystal: $\alpha(P_L,h\omega) = \alpha_0(h\omega) (1 - \rho_n V_{\text{blockade}})$. Vice versa, the exciton density $\rho_n$ is determined by this absorption $\alpha$ times the laser power $P_L$ deposited within the exciton lifetime $\tau_n \propto 1/\Gamma_n$ in the crystal: $\rho_n \propto P_L \alpha / \Gamma_n$. Inserting this relation for the exciton density and solving for the absorption $\alpha$ allows us to derive the following scaling law for the dependence on laser power:

$$\alpha(P_L,h\omega) = \frac{\alpha_0(h\omega)}{1 + S_n P_L}.$$ 

**Figure 3 | Reduction of excitonic absorption due to dipole blockade.**

a. Absorption spectra measured with different laser intensities. We note the quenching of the high-$n$ resonances when applying stronger laser excitation. b. Dependence of oscillator strength (peak area) on laser power for different $n$ resonances; solid lines show $\frac{A}{1 + S_n P_L}$ fits to the data. c. Dependence of blockade efficiency $S_n$ on laser power; solid line shows the fit according to $n^{10}$ dependence. d. Absorption spectra in the two-beam experiment. The energy of the pump laser was fixed at $n = 14$. e. Change of absorption at $n = 17$ resonance in the two-beam experiment as a function of the pump laser photon energy (pump intensity $0.3 \text{ mW mm}^{-2}$). The red line is a guide for the eye. The grey line presents a single-beam absorption spectrum in this energy range, proving that the absorption is quenched more strongly when the pump laser is tuned to an exciton resonance. We note the slight line shifts between the resonances in the two spectra arising from exciton–exciton interaction. Owing to the variation of the exciton separation in the laser spot, these shifts cannot be assessed quantitatively, for which one would have to control the exciton position. f. Influence of a magnetic field on the Rydberg blockade. Shown are the optical densities at $B = 0 \text{T}$ and $B = 0.8 \text{T}$ as functions of excitation intensity.
where \( S_n \) describes the efficiency with which the absorption at the energy of exciton state \( n \) is blocked through the presence of excitons in the same state. Equation (1) describes the observed dependencies well; see Fig. 3b. By fitting the experimental data for the peak area, we can extract the \( S_n \) values that are shown from \( n = 12 \) up to 24 in Fig. 3c. In this high-\( n \) range, \( S_n \) varies enormously, with the principal quantum number increasing by more than three orders of magnitude. By fitting the data with a power function, we find a dependence on the tenth power of \( n \).

To understand the strong \( n \)-dependence, one has to consider possible dipole–dipole interaction mechanisms. At large separations they can be modelled by a van der Waals interaction energy \( E_{\text{dvw}}(n) = -C_6(n)/R^6 \), where \( R \) is the distance between two P-excitons in state \( n \). For smaller distances the interaction becomes resonant and is better described by a Förster-type dependence \( E_F(n) = -C_3(n)/R^{3+} \). One finds that \( C_6 \) varies with the principal quantum number as \( n^4 \), while \( C_3 \) scales as \( n^4 \) (for details, see Supplementary Information). The onset criterion for the blockade of the dipole interaction becomes larger than the absorp- tion linewidth leads to a critical blockade radius \( R_c(n) = \sqrt{C_6(n)/\Gamma_n} \). From this radius the blockade volume \( V_{\text{blockade}} = 4/3\pi R_c^3 \) can be derived.

Taking the above considerations into account, we conclude that the dependence of the blockade efficiency \( S_n \) on the principal quantum number \( n \) is determined by the product of blockade volume \( V_{\text{blockade}} \) times the exciton lifetime \( \tau_n \propto 1/\Gamma_n \). From \( V_{\text{blockade}} \propto R_c^3 \propto n^3 \) for both mechanisms of dipolar interaction and \( \Gamma_n \propto n^{-3} \) we obtain an extremely steep increase in the blockade efficiency \( S_n \) with increasing principal quantum number, given by its tenth power: \( S_n \propto \sqrt{\Gamma_n} \propto n^{10} \), in excellent agreement with experiment.

We expect the Coulomb blockade to occur only not for excitons with the same \( n \), but also for different \( n \). In effect, the experiment thus far resembled a single-beam pump–probe experiment with degenerate pump and probe. To test our suggestion further, we implemented another tunable laser with a linewidth of 1 neV (about 250 kHz in frequency) so that we could vary the pump and probe photon energies independently. At first, we kept the photon energy of the pump laser fixed at the exciton Bohr radius, for example, is much larger for similar principal quantum numbers, so that comparable blockade volumes may be reached for excitons at considerably smaller \( n \) than for atoms. In addition, the light wavelength is shrunk in the \( \text{Cu}_2\text{O} \) crystal by the refractive index of 3, so that Rydberg excitons permit testing of light–matter interaction descriptions, such as the electric-dipole approximation. Differences may also show up in studies of interaction effects among excitons, which may be deliberately induced and controlled by exciting additional excitons in particular \( n \) states. The relaxation of excitons by phonons may lead to the formation of low-\( n \) exciton populations with which the Rydberg excitons can interact. One of these excitons, the paraelectron, is a prime candidate for Bose–Einstein condensation in \( \text{Cu}_2\text{O} \) (ref. 15), so that recent experiments in atomic physics\(^6\) could be mimicked by studying the interaction of a Rydberg exciton with such a condensate.

Despite a long-standing discussion\(^6\), molecules formed from two excitons have not previously been demonstrated in \( \text{Cu}_2\text{O} \). Rydberg excitons open up new perspectives owing to their strong dipole–dipole interactions\(^7\). Exciton molecules with varying constituents and tunable binding energies could be excited\(^8\)–\(^11\). The number of excitons forming a molecule may be varied to form large cluster-like states or extended condensed phases.

The crystal environment means that Rydberg excitons could permit studies that are not possible in atomic physics. For example, the position of individual Rydberg excitons might be accurately controlled by applying spatially modulated strain fields to the crystal. Also, additional electric or magnetic fields may be applied, with which the interaction between Rydberg excitons and their stability could be dynamically controlled. Rydberg atoms subjected to high magnetic fields mimic hydrogen atoms (ref. 22 and references therein) in white dwarf stars. Such a hydrogen-like system in a strong magnetic field represents a non-integrable problem leading to chaotic behaviour. Rydberg excitons have smaller Rydberg energies, so they should enter a similar regime at very low magnetic fields, which are easier to study.

Received 5 March; accepted 2 September 2014.

1. Gallagher, T. F. Rydberg atoms. Rep. Prog. Phys. 51, 143–198 (1988).
2. Knox, R. S. Theory of Excitons (eds Ehrenreich, H., Seltz, F. & Turnbull, D.) Solid State Phys. Suppl. Vol. 5 (Academic, 1965).
3. Gross, E. F. Optical spectrum of excitons in the crystal lattice. Nuovo Cimento Suppl. 3, 672–701 (1956).
4. Gross, E. F. & Karyjew, I. A. The optical spectrum of the exciton. Dokl. Akad. Nauk. SSSR 84, 471–474 (1952).
5. Elliott, R. J. Intensity of optical absorption by excitons. Phys. Rev. 106, 1384–1389 (1957).
6. Matsumoto, H., Saito, K., Hasuo, M., Kono, S. & Nagasawa, N. Revived interest on yellow-exciton series in Cu2O: an experimental aspect. Solid State Commun. 97, 125–129 (1996).
7. Saffman, M., Walker, T. G. & Melzer, K. Quantum information with Rydberg atoms. Rev. Mod. Phys. 82, 2313–2363 (2010).
8. Balewski, J. B. et al. Coupling a single electron to a Bose–Einstein condensate. Nature 502, 664–667 (2013).
9. Kiffner, M., Park, H., Li, W. & Gallagher, T. F. Dipole-dipole-coupled double-Rydberg molecules. Phys. Rev. A 86, 031401(R) (2012).
10. Boisseau, C., Simbotin, I. & Côté, R. Macrodimers: ultralong range Rydberg molecules. Phys. Rev. Lett. 88, 133004 (2002).
11. Bendkowsky, V. et al. Observation of ultralong-range Rydberg molecules. Nature 458, 1005–1008 (2009).
12. Varga, K., Usukura, J. & Suzuki, Y. Second bound state of the positronium molecule and biexcitons. Phys. Rev. Lett. 80, 1876–1879 (1998).
13. Cassidy, D. B. & Mills, A. P. Jr. The production of molecular positronium. Nature 449, 195–197 (2007).
14. Friedrich, H. & Wintgen, D. The hydrogen atom in a uniform magnetic field—an example of chaos. Phys. Rep. 183, 37–79 (1989).

Supplementary Information is available in the online version of the paper.

Acknowledgements We thank R. Höng for experimental support with the first measurements. We acknowledge financial support by the Deutsche Forschungsgemeinschaft (BA 1549/18-1 and SFB 652 Strong correlations and collective effects in radiation fields). M.B. acknowledges support from the Russian Ministry of Science and Education (contract number 14.250.31.0021).

Author Contributions T.K., D.F. and M.B. conceived, designed and carried out the experiments. H.S. and S.S. contributed through the Rydberg blockade model. All authors cooperated in data analysis, discussions and preparation of the manuscript.

Author Information Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper. Correspondence and requests for materials should be addressed to D.F. (dietmar.froehlich@tu-dortmund.de).