level. It should be stressed, also, that the susceptibility of the system $Ce(Ir_xOs_{1-x})_2$ is relatively small which is not very "typical to ICF systems" and somewhat inconsistent with our VBS picture.

In summary, the lattice-constant study indicates that mixtures in the vicinity of $CeIr_2$ exhibit intermediate-valence state of the cerium (Fig. 1). On the assumption that the Ce $4f$ state can be described by a VBS model, the ESR properties support the idea of intermediate-valence state. Preliminary susceptibility study[9] is not completely consistent with this interpretation. This might indicate that our VBS picture is somewhat naive and that further experiments like x-ray-photoemission spectroscopy as well as theory are needed. Our work clearly indicates, however, that the narrowing mechanism of Gambke, Elschner, and Hirst[7] is not typical to ICF systems.

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Evidence for Bose-Einstein Statistics in an Exciton Gas

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A free-exciton gas is studied as a function of generated particle density in Cu_2O at 1.5 K. A line-shape analysis of the subsequent recombination shows a gradual evolution, from a classical regime at low density, to a highly quantum-statistical one with chemical potential $\mu \simeq 0$.

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It is well known that in an ideal Bose gas the energy distribution of the particles obeys the relation

$$N(E) = \rho(E) f(E), \tag{1}$$

where $\rho(E) = AE^{1/2}$ is the density of states, $f(E) = \{\exp[(E-\mu)/KT] - 1\}^{-1}$ is the occupation number of levels of energy E, measured from the lowest level $E=0$, and μ is the chemical potential of the gas, determined by the condition that $\sum_E N(E) = N_t$, the total number of particles. In usual situations, the ratio $-\mu/KT \gg 1$ and relation (1) is very well approximated by Maxwell-Boltzmann distribution. If $-\mu/KT < 2$, differences from classical statistics occur, with a tendency for the particles to accumulate in the states of lowest energy. This quantum attraction effect becomes precipitous if $N_t > N_c = 6.2 \times 10^{15} g(m/m_0)^{3/2} T^{3/2}$ (m_0, free-electron mass; m particle mass; g, degeneracy factor), for which $\mu = 0$, giving rise to a phase transition with a macroscopic occupation of a single quantum state $E=0$ [Bose-Einstein condensation (BEC)]. It is generally admitted that BEC is the physical origin of the spectacular properties of ^4He below the λ point although an interpretation using the ideal Bose gas as a starting point raises serious questions, because of the strong interactions between atoms in liquid helium. It is therefore important to search for new, more dilute Bose systems, in which purely statistical effects are predominant, and where interparticle interactions may be treated as a small perturbation.

The purpose of this Letter is to present experimental evidence which indicates that a gas of free excitons may indeed manifest the quantum-statistical behavior characteristic of a dilute Bose gas.[1] Cu_2O has several characteristics which are necessary for BEC of excitons. These characteristics are *not found* in most other crystals, and thus prevent the observation of this effect despite the fact that the required excitation conditions have been available for several years.[2] A first condition is the presence of an overall repulsive exciton-exciton potential. If excitons attract each other in real space, the theory of a weakly nonideal Bose gas does not apply;[3] instead, new collective excitations, like excitonic molecules or electron-hole drops, are formed at increasing particle densities. Bassani and Rovere[4] have shown that in Cu_2O the pair potential is repulsive, because of the strong electron-hole exchange interaction and nearly equal electron and hole effective masses ($\sigma = m_e/m_h \simeq 0.7$). Another prerequisite is a weak exciton-photon coupling since otherwise the polariton effect would prevent an accumulation of the particles at the bottom of their kinetic-energy band.[5] In Cu_2O the even-parity S-like excitons of the yellow series do not interact in the dipole approximation with the radiation field because of parity conservation. Finally, the exciton radius a_x must be small, because of the occurrence of a Mott dissociation of excitons, if $Na_x^3 \simeq 0.3$. In Cu_2O, $a_x < 10$ Å so that even at densities well above $N_c \sim 10^{19}$ cm^{-3} at 20 K a dissociation of excitons into a plasma is unlikely.

Optically generated electron-hole pairs in Cu_2O relax quickly towards the $n = 1$ term of the lowest (yellow) excitonic series. The $n = 1$ term of the series is split by e-h exchange into a triply degenerate Γ_{25}^+ orthoexciton ($X_o = 16\,403$ cm^{-1} at 1.5 K) and a paraexciton Γ_2^+ ($X_p = 16\,307$ cm^{-1} at 1.5 K). In pure samples[6] the lifetime of the orthoexciton is limited by ortho-para conversion. The paraexciton, on the other hand, has a very long lifetime ($\tau \sim 10$ μs at 15 K).[7] It is therefore logical to search for degeneracy effects on the paraexciton population, since high densities ($n \sim 10^{17}$ cm^{-3}) are already obtained with moderate cw optical excitation.[7] However, as we increased the excitation intensity beyond that reported in Ref. 7 with use of a N_2-laser–pumped dye laser ($I_{max} \sim 10^7$ W/cm^2), an important sublinear behavior of the paraexciton emission intensity was observed. We will comment on this below. By contrast, the orthoexciton emission was found to be still linear in the same intensity range. We therefore concentrated our attention on the behavior of orthoexcitons.[8] The radiative decay of the $n = 1$ orthoexcitons occurs predominantly with simultaneous emission of a parity-conserving phonon Γ_{12}^-(106 cm^{-1}). The line shape of this decay process provides a very convenient measure of the velocity distribution of the free-exciton gas, since it is given by expression (1).[9] We have verified this law to be very well satisfied at low excitation in-

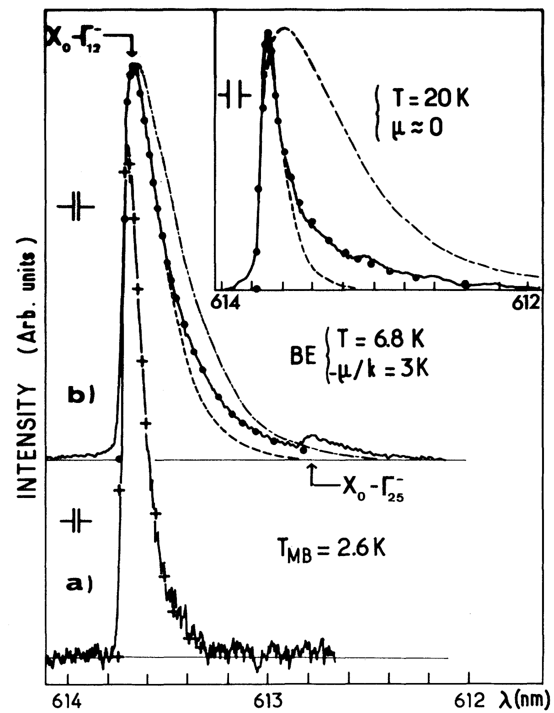

FIG. 1. Line shapes of the phonon-assisted recombination of orthoexcitons (X_o-Γ_{12}^-) in Cu_2O at bath temperature $T = 1.5$ K. (a) Low-intensity cw Ar^{++}-laser excitation ($\lambda = 514.5$ nm; $I_0 \sim 10^2$ W/cm^2). (b) Same conditions as (a) except for the laser intensity, which is increased by a factor of 14. Inset: pulsed-dye-laser excitation ($\lambda = 598$ nm; $I_0 \sim 10^7$ W/cm^2). Circles are calculated line shapes, taking Bose-Einstein distribution with μ and T as indicated, convoluted by the spectral response of the detection (resolution as shown). Crosses in (a) correspond to a convoluted Maxwell-Boltzmann line shape. The dashed lines are Maxwell-Boltzmann functions either of same half width as the experimental curve, or with $T = T$(Bose-Einstein), to show the deviations from classical behavior. The small structure at 612.8 nm corresponds to the X_o-Γ_{25}^- phonon-assisted emission line.

tensity over a wide temperature range $1.5 < T < 150$ K, provided that a Maxwell-Boltzmann relation $f(E) = \exp(-E/KT)$ is introduced.

This is no longer the case at 1.5 K, where a *gradual* deviation from the classical distribution is observed with increasing input intensity I_0 (see Fig. 1). These deviations are connected with the generated electron-hole pair densities rather than input light intensities. For instance, for the same cw intensity ($I_0 \sim 10^4$ W/cm^2) they are pronounced at an excitation wavelength $\lambda = 514.5$ nm (Ar^{++} laser) but are not apparent if $\lambda = 600$ nm (cw dye laser), for which the absorption coefficient of the crystal $\alpha \simeq 40$ cm^{-1} is smaller by a factor of 40. They reappear, however, if the excitation at $\lambda = 600$ nm is increased by orders of magnitude (N_2-laser-pumped rhodamine 6G dye laser). The experimental luminescence line shapes may be explained in a straightforward manner, by introducing the distribution function (1) valid for Bose particles at high density (see Fig. 1).[10]

In Fig. 2 we plot $-\mu/KT$ and ΔT, the temperature increase of the exciton gas as a function of I_0, for an excitation range which includes the classical limit.[11] Also shown in the same figure is the density N_t of particles deduced from the line-shape analysis by integrating expression (1) with μ and T deduced from a best fit, taking $m = 3m_0$ (Ref. 12) and $g = 3$ for the triplet state. It is worthwhile to mention that this method of extracting a particle density is very powerful, because it does not require any knowledge of poorly known parameters such as the excited volume in the sample or the lifetime of particles.[13] Note the linear dependence of N_t with I_0, which indicates that no appreciable volume expansion of the exciton gas takes place with increasing N_t (at least in this density range), as expected for a gas with weak interactions. Exciton densities extracted from data obtained with different excitation conditions are shown in Fig. 3, together with the variation of N_c vs T predicted by the ideal-Bose-gas model. As it can be seen, the particle density increase is accompanied by a substantial heating of the gas, making it difficult to reach the critical value N_c. Despite this fact, a complete set of densities is obtained, up to N_c around $T \sim 20$ K.[14]

Finally we return to the problem of the paraexciton emission line and consider the following kinetics equations, in which a destruction term

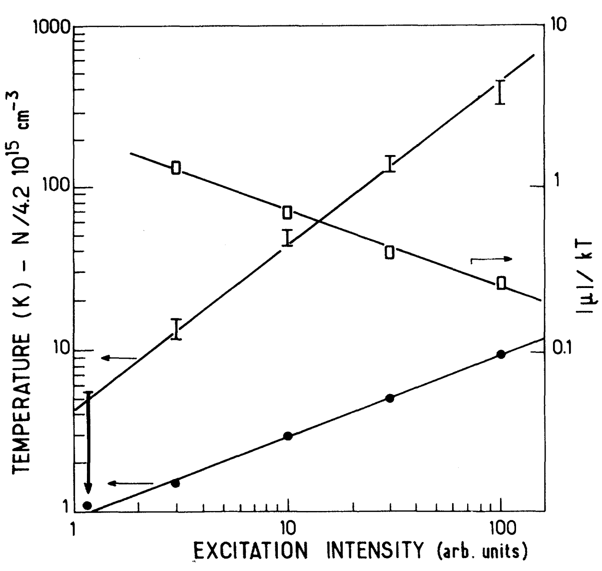

FIG. 2. Temperature increase ΔT (black dots), $|\mu|/KT$ (open rectangles), and density of orthoexcitons (vertical bars) as function of incident Ar^{++}-laser intensity, as deduced from best fits of $X_o - \Gamma_{12}^-$ line-shape analysis at $T = 1.5$ K. The density of particles at the lowest I_0 is undetermined, since it fits a Boltzmann distribution; the upper limit of N compatible with the line shape is shown.

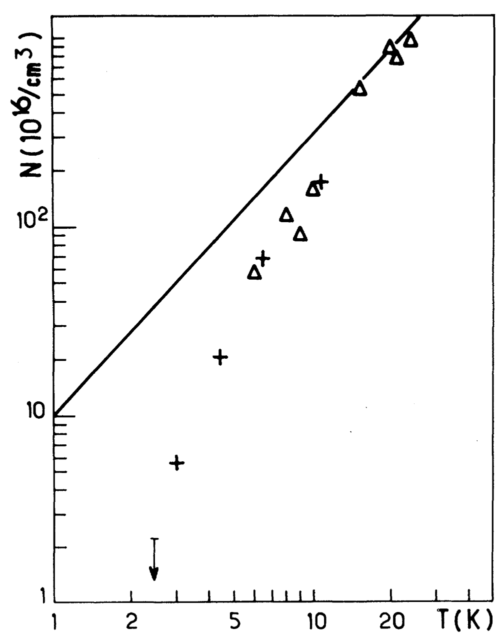

FIG. 3. Density of orthoexcitons as function of particle effective temperature. Crosses are from Ar^{++}-laser excitation, triangles from N_2-laser-pumped dye-laser excitation at $\lambda = 598$ nm. The straight line of slope 1.5 gives the orthoexciton critical density for Bose-Einstein condensation, in the ideal-Bose-gas model.

proportional to the particle collision rate is introduced:[15]

$$\dot{X}_o = -(\gamma + \gamma_t)X_o + aI - CX_o(X_o + X_p),$$

$$\dot{X}_p = +\gamma_t X_o - \gamma X_p - CX_p(X_o + X_p).$$

X_o and X_p refer to the orthoexcitons and paraexcitons, γ_t is the ortho-para transfer rate, γ is the inverse exciton lifetime in absence of ortho-para transfer and collisions, a is the quantum yield for exciton formation, and C is a collision coefficient. Taking $C \sim 10^{-11}\ \text{cm}^3\ \text{s}^{-1}$, $a \sim 1$, $\gamma_t \sim 10^{7-8}\ \text{s}^{-1}$, and $\gamma \ll \gamma_t$, as deduced from Ref. 7, the steady-state solution predicts a behavior compatible with our results within a large intensity range $1\ \text{W/cm}^2 < I(\lambda \simeq 600\ \text{nm}) < 3\times 10^5\ \text{W/cm}^2$, for which X_o still varies linearly with I, whereas X_p has a sublinear-law dependence with an exponent ~ 0.5 or less.

In conclusion, it has been shown that a gas of free excitons exhibits the quantum-statistical properties expected from a gas of ideal Bose particles at high densities.

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[6] The results reported here were obtained in very pure crystals of natural growth. Similar experiments performed on synthetic crystals of lesser quality (as evidence by a smaller exciton luminescence efficiency) did not lead to the same effects.

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[8] The overlap of the paraexciton emission line $X_p - \Gamma_{25}^-$ with the orthoexciton line $X_o - X_{15}^-$ prevented us from studying the line shape $X_p - \Gamma_{25}^-$ at much higher intensities than those reported in Ref. 7.

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[10] Note the temperature increase of the exciton gas. An effective temperature for the excitonic particles higher than the lattice T is a common feature of many strongly excited crystals. It is due to the excess energy delivered to the system in the pumping process and indicates that complete thermalization of the gas with respect to the lattice is not reached during the particle lifetime. One might object that the deviations reported here result from the superposition of Maxwell-Boltzmann functions with different temperatures, the temperature gradient being related to an exciton-density gradient. In order to evaluate this possibility, we have performed several computer simulations of line shapes, taking various temperature gradients. It was not possible to reproduce any of the experimental results if it is assumed that regions of higher densities (and consequently higher T) have higher *luminosity.* (We have verified this assumption by recording emission spectra from various parts of the excited sample surface. As expected, the most intense luminescence comes from the central part of the excited spot with spectra as reported here.)

[11] The variation of I_0 shown here was obtained under identical experimental conditions except for neutral-density filters in front of the laser. This procedure is possible with light sources of high average power, such as cw argon laser ($P \sim 1$ W), but not with our N_2-laser–pumped dye laser ($P \sim 10^{-3}$ W). In the latter case, however, defocusing of the laser spot on the sample leads to a decrease of μ.

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[13] An evaluation of the exciton density from the experimental conditions with an exciton lifetime $\tau \sim 10^{-8}$ s (Ref. 7) leads to the same order of magnitude.

[14] At the present time we have no satisfactory explanation for the fact that N apparently approaches $N_c(T)$ asymptotically. As noted before, this is related to the excess energy ΔE supplied by the pumping photons. We have tuned the exciting laser to the position of the narrow quadrupole absorption line X_o at 609.6 nm, thereby minimizing ΔE; the $X_o - \Gamma_{12}^-$ spectrum in that case exhibits a sharp emission peak at 613.70 nm, as is expected from a Bose condensate with $N \gg N_c$. However, this sharp peak is also present under weak excitation intensity (for which N_c should not be reached) and can therefore be attributed to a resonant Raman effect [R. M. Habiger and A. Compaan, Phys. Rev. B 18, 2907 (1978)].

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