an enhanced population of the ground state of the crystal field. However, to account for the very short T_2^{intra} observed a crystal field of nearly 2 K would be required, which is rather large compared to the value estimated from the T_1 data. The low-concentration T_2 data thus still remains to be explained.

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Evidence of the Autoionizing Character of Biexcitons

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The highly structured profile of the Γ_1 biexciton level of CuCl is studied experimentally by resonant coherent nonlinear scattering. A theoretical model is presented which accurately describes the Γ_1 biexciton line shape in terms of a Fano interference, evidencing the autoionizing character of biexcitons.

In a previous Letter[1] we have reported the direct observation of the excitonic molecule level in cuprous chloride by a resonant coherent and degenerate nonlinear light scattering. In this process the interaction between "pump" and "test" beams in a thin slab of CuCl gives rise to the third-order polarization,

$$\vec{P}_s(\omega)=\epsilon_0\chi^3(-\omega;\omega,\omega,-\omega)\vdots\vec{E}_p(\omega)\vec{E}_p(\omega)\vec{E}_t^*(\omega), \quad (1)$$

which in turn radiates a collimated "signal" beam in the direction $\vec{k}_s=2\vec{k}_p-\vec{k}_t$ [the notations of Ref. 1 have been used]. This type of spectroscopy has revealed two features of the biexciton level unsuspected so far: (i) the very asymmetric line shape of the resonance and (ii) the highly nonlinear power dependence of the scattering.

The present Letter concentrates on the unusual line shape of the first-order scattering. New experimental data and a theory are presented. This latter explains the observed asymmetric line shape of the biexciton level in terms of a Fano interference.[2]

A detailed description of the experiment is given elsewhere.[3] Compared to the data presented in Ref. 1, a highly improved signal/noise ratio has been obtained by use of a double synchronous detection method. Typical recordings of the ratio $\rho=I_s(l)/I_t(0)$ of the outgoing signal beam intensity to that of the incoming test beam as a function of the dye-laser frequency are shown in Fig. 1(a) and 2(a), respectively, for two high-purity CuCl samples with thicknesses $l=80$ μm and $l=200$ μm. Both exhibit a sharp dip at $\hbar\omega=3.1860$ eV, i.e., half the energy of the biexciton W_{X2} as observed in two-photon absorption[4] (TPA); this dip is surrounded by two humps, about 1.5×10^{-3} eV apart,

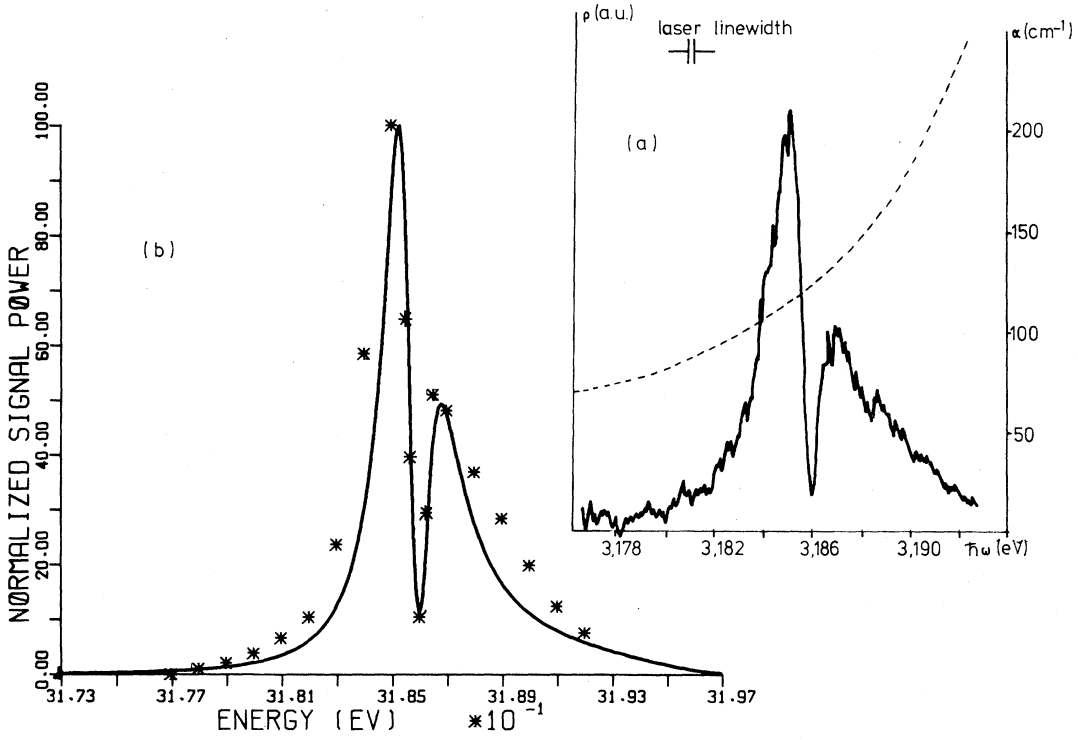

FIG. 1. (a) Frequency dependence of the first-order scattering in a 80-μm thick sample with $I_p(0) = 20I_t(0) = 10$ MW/cm^2. (b) Comparison of the theory (solid line) and the experimental data of (a) (stars).

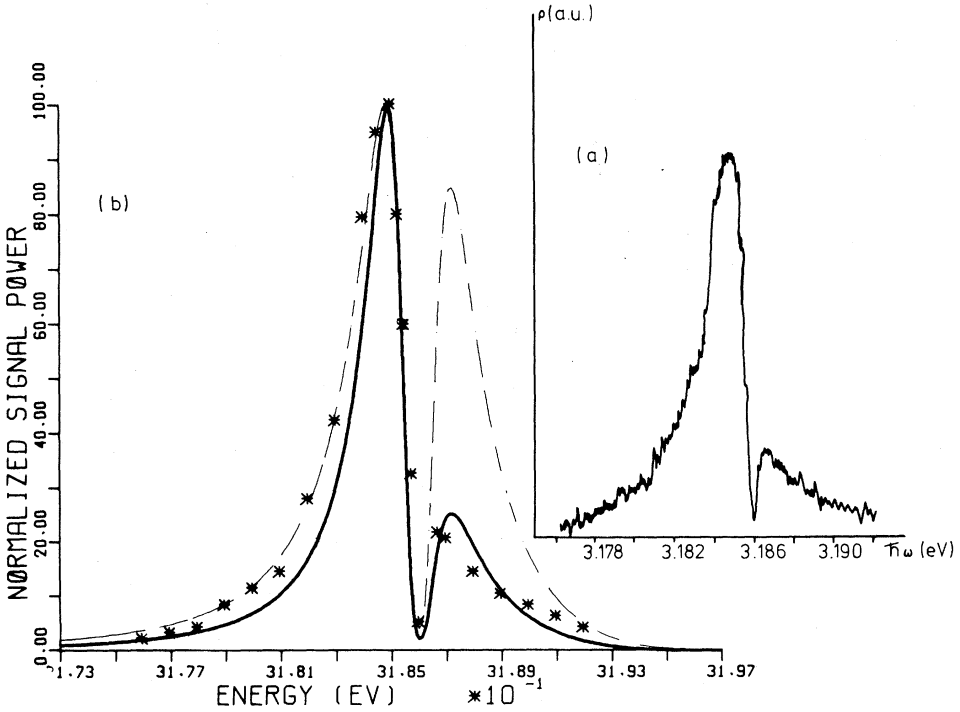

FIG. 2. (a) Frequency dependence of the first-order scattering in a 200-μm-thick sample with $I_p(0) = 20I_t(0) = 15$ MW/cm^2. (b) Comparison of the experimental data of (a) (stars) and the theory: autoionizing model, solid line; isolated-level description, dashed line.

the height of the high-energy-side maximum being approximatively 50% and 20% of that of the low-energy one for the thin and the thick samples, respectively.

Since the relative variations of the linear absorption coefficient, α, are very small in that energy range, one expects for ρ an almost symmetric line shape. This point is most easily seen on its analytical expression in the parametric approximation,[1] which corresponds fairly well to the experimental conditions in which the curves of Figs. 1(a) and 2(a) were obtained [$I_p(0) = 20 I_t(0)$]:

$$\rho = e^{-\alpha l}(\tfrac{1}{2}|\kappa| I_p(0) l_a)^2 (1 + \kappa_2 I_p(0) l_a)^{-3}, \qquad (2)$$

where $l_a = \alpha^{-1}(1 - e^{-\alpha l})$ is the effective interaction length due to the linear absorption ($l \leq l_\alpha \leq \alpha^{-1}$) and $\kappa = \kappa_1 + i\kappa_2 = \omega\chi^{(3)}(\epsilon_0 n^2 c^2)^{-1}$.

For a system of isolated levels, the third-order susceptibility describing a process dominated by the two-photon resonance on the biexciton ($X2$) and the one-photon quasiresonance on the exciton (X) is written as[5]

$$\chi_{IS}^{(3)}(-\omega;\omega,\omega,-\omega) \propto \frac{|\langle g|\mu|X\rangle|^2 |\langle X|\mu|X2\rangle|^2}{(W_X - i\Gamma_X - \hbar\omega)^2 (W_{X2} - i\Gamma_{X2} - 2\hbar\omega)}, \qquad (3)$$

where $|g\rangle$ is the ground state and μ the dipole moment. In the vicinity of $\hbar\omega = \frac{1}{2} W_{X2}$ it exhibits a Lorentzian resonance and thus the variation of ρ should go, with increasing intensity from a Lorentzian peak to a symmetric camel-back-shaped resonance, modulated by a smooth envelope reflecting the variations of α. This in in evident contradiction with the experimental facts. To explain the observed profile, one can think of some polariton effects but the large value of the longitudinal-transverse splitting in CuCl ($\Delta_{LT} = 5.5\times10^{-3}$ eV[6]) rules out this hypothesis. The sole possibility left is that TPA is larger on the high-energy side of the resonance than on the low-energy one. Such a behavior suggests that $\mathrm{Im}(\chi^{(3)})$ presents a structure in close analogy with that of $\mathrm{Im}(\chi^{(1)})$ near a one-photon resonance of an autoionizing (AI) state, because of Fano interference.

The biexciton is usually considered as a bound state by reference to two unrelated excitons —that is, if its energy is lower than twice that of the exciton. However, the biexciton spontaneously decays into other elementary excitations of the crystal.[7] Hönerlage, Bivas, and Pache[6] have recently identified the most probable recombination paths of biexcitons in CuCl as $X2 \rightarrow P_1(q) + P_1(k)$ or $P_1(q) + P_u(k)$ or $P_1(q) + X_L(k)$, where $P_{l,u}$ represent the lower and upper polariton branches and X_L a longitudinal exciton. In the two-elementary-excitation configuration states, the unrelated pairs of elementary excitations form a continuum $|c(\epsilon)\rangle$ overlapping the energy of the biexciton and coupled to it.

AI effects in nonlinear optics have been discovered and investigated on metallic atomic vapors by Armstrong and Wynne.[8] The vacuum AI states involved in their experiments are connected to the ground state by dipole-allowed transitions. In Fano's description,[3] the coupling of the continuum $|c(\epsilon)\rangle$ and the modified discrete state $|X2\rangle$ results in a new state

$$|b(\epsilon)\rangle = (\sin\Delta/\pi V_\epsilon)|X2\rangle - \cos\Delta|c(\epsilon)\rangle,$$

in the notations of Ref. 3.

The transition moment between a discrete state $|X\rangle$ and the AI state $|b(\epsilon)\rangle$ is described by the dimensionless Fano's "q parameter": $q = \langle X2|\mu|X\rangle \times [\pi V_\epsilon \langle c(\epsilon)|\mu|X\rangle)^{-1}$, which is infinite in the case of null coupling. Then the third-order susceptibility can be written as

$$\chi_{AI}^{(3)}(-\omega;\omega,\omega,-\omega) \propto \int \frac{|\langle g|\mu|X\rangle|^2 |\langle X|\mu|b(\epsilon)\rangle|^2 d\epsilon}{(W_X - i\Gamma_X - \hbar\omega)^2 (\epsilon - i\gamma - 2\hbar\omega)}.$$

To evaluate this integral we used the contour method of Armstrong and Wynne[8] with the following energy scale: $\epsilon \rightarrow (\epsilon - W_{X2})/(\pi|V_\epsilon|^2)$. It is found that

$$\chi_{AI}^{(3)}(-\omega;\omega,\omega,-\omega) \propto \frac{|\langle g|\mu|X\rangle|^2 |\langle X|\mu|X2\rangle|^2}{(W_X - i\Gamma_X - \hbar\omega)^2 (W_{X2} - i\Gamma_{X2} - 2\hbar\omega)} \left\{1 - \frac{2i}{9} + i\frac{W_{X2} - 2\hbar\omega}{9^2 \Gamma_{X2}}\right\}, \qquad (4)$$

where we have identified the linewidth of the observed resonance with that arising from the coupling to the nearby continuum and neglected other relaxations ($\Gamma_{X2} \simeq \pi|V_\epsilon|^2\rangle\rangle\gamma$). This form generalizes the usual one, i.e., Eq. (3), which is obtained from Eq. (4) by letting $q \rightarrow \infty$. For any finite value of q, $|\chi_{AI}^{(3)}|$ and

$|\chi_{IS}^{(3)}|$ are equal up to the second order in q^{-1}, but both $\mathrm{Im}(\chi_{AI}^{(3)})$ and $\mathrm{Re}(\chi_{AI}^{(3)})$ have an asymmetric structure. For instance, near a two-photon resonance $\mathrm{Im}(\chi_{AI}^{(3)}) \propto (\epsilon+q)^2(\epsilon^2+1)^{-1}$ has a zero minimum at $\epsilon=-q$ and a maximum at $\epsilon=q^{-1}$, both of which do not coincide with those of $|\chi_{AI}^{(3)}|$.

It is, however, rather difficult to identify such a structure amidst a large linear absorption. Conversely, in active spectroscopy where the observed signal results from the competition between the nonlinear gain $\{[\frac{1}{2}|\kappa| I_p(0) l_a]^2\}$ and the TPA $\{[1+\kappa_2 I_p(0) l_a]^{-3}\}$ the differences between the two profiles are readily displayed.

In order to analyze our data without any approximation, we have solved numerically the set of six coupled differential equations describing the scattering[9] and used visual fitting procedure. The inputs were the intensities the thickness; $\alpha(\omega)$ and $\chi_{AI}^{(3)}$, the fitting parameters being g, Γ_{X2}, and the ratio of the exciton-biexciton transition probability to the ground-state–exciton one[10]: $[g(0)/\sqrt{\Omega}]^2 = |\langle X|\mu|X2\rangle|^2 \; |\langle X|\mu|g\rangle|^{-2}$, where Ω is the volume of the unit cell. *For both thicknesses and all intensities an excellent fit was obtained with the same set of fitting parameters:* $q=15$, $\Gamma_{X2}=5\times10^{-4}$ eV, and $[g(0)/\sqrt{\Omega}]^2=1000$. This is shown in Figs. 1(b) and 2(b), where the solid curves correspond to the best fit and the stars to the experimental data of Figs. 1(a) and 1(b). It is worth noticing that it was impossible to find any reasonable fit with the isolated-level description [dashed line in Fig. 2(b)], and that the parametric approximation analytical solution, Eq. (2), was found to follow closely the full system one as long as $I_p(0) > 5 I_t(0)$. To the best of our knowledge our observation is the first unambiguous one relative to a dipole-forbidden AI state. Our value of $[g(0)/\sqrt{\Omega}]^2$ is in satisfactory agreement with that (300) deduced by Phach *et al.*[4] from TPA measurement.

Theoretical estimates are usually expressed in terms of $A=|\varphi_{1s}(0)g(0)|^2$ where $\Phi_{1s}(\boldsymbol{r})$ is the exciton envelope function, which is rather inaccurately known in CuCl. Nevertheless, retaining for the exciton radius a usually admitted value of $a_X=7$ Å, our experimental results yield $A=37$, in agreement with the theoretical values of Arya and Hassan[11] ($A=50$) and Ekardt and Sheboul[12] ($A=20$) but in disagreement with Hanamura[13] ($A=10^3$). As for the linewidth, it may be slightly overestimated because it is just twice larger than that of our laser ($\hbar\,\delta\omega=2.5\times10^{-4}$ eV). The large value of q indicates a weak coupling to the continuum, reflecting the partial photonlike nature of the elementary-excitation pairs associated with it. However it so happens that comparable values have been found in one-photon atomic spectra.[14]

Some improvements can be brought to our description, by using the full expression of $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$, including 24 terms for the three leading levels and a smooth background for the others. It should be noted that since some of these terms are resonant on the exciton, their inclusion may improve the fit on the high-energy side. However it is a small modification which does not modify the results established in this Letter.

In conclusion, using an original method we have seen for the first time a two-photon autoionizing state in a solid. We have also presented a theoretical model describing accurately the nonlinear optical behavior of this state and thus we have unambiguously shown the autoionizing character of biexcitons.

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Note added.—Since the submission of this paper, it has come to our attention that in the work of R. Y. Chiao, P. L. Kelly, and E. Garmire [Phys. Rev. Lett. 17, 1158 (1966)], and of R. L. Carman, R. Y. Chiao, and P. L. Kelly [Phys. Rev. Lett. 17, 1281 (1966)] a method similar to ours has been used, although for a completely different purpose.

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Electromagnetic Effects near the Superconductor-to-Ferromagnet Transition

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Electromagnetic effects are shown to govern the transition from superconductivity to ferromagnetism. A first-order transition to uniform ferromagnetism is predicted generally, but preceded by magnetic critical scattering which peaks at a finite wave vector.

Superconductors containing a periodic lattice of magnetic rare-earth ions have recently been discovered.[1,2] In some of them, as the temperature is decreased the superconducting state is followed by a transition to a ferromagnetic state[3] in which superconductivity disappears.

The theory of superconductors containing magnetic ions has been extensively studied,[4] particularly the effects of spin-flip scattering and conduction-electron polarization. Here we consider the effects of the interaction between the macroscopic magnetization $\vec{M}$, the electromagnetic field $\vec{A}$, and the superconducting order parameter $|\psi|$ and show that near the ferromagnetic transitions they play a dominant role in type-II superconductors.

We find that transitions from the superconducting state to two different states are possible as the temperature is decreased: a state of uniform magnetization which is not superconducting and a superconducting state in which the magnetization is oscillatory (spiral structure) at a wave vector of the order of $(\gamma\lambda)^{-1/2}$, where γ is the magnetic stiffness length and λ is the London penetration depth. For a reasonable choice of parameters, a first-order transition to the former is predicted, as is experimentally observed. This transition is, however, always preceded by a region of temperature in which $\chi(q)$, the wave-vector–dependent susceptibility, peaks at a finite wave vector, indicating a tendency toward the spiral state.

Our starting point is the free-energy functional:

$$F\{\psi,\vec{M},\vec{A}\}=\int d^3r\{\tfrac{1}{2}a|\psi|^2+\tfrac{1}{4}b|\psi|^4+p_0|(\nabla-ir_0\vec{A})\psi|^2 + (\vec{B}^2/8\pi)+\tfrac{1}{2}\alpha|\vec{M}|^2+\tfrac{1}{4}\beta|\vec{M}|^4+\tfrac{1}{2}\gamma^2|\nabla\vec{M}|^2-\vec{B}\cdot\vec{M}+\tfrac{1}{2}[\eta_1\vec{M}^2+\eta_2|\nabla\vec{M}|^2]|\psi|^2\}. \quad (1)$$

In Eq. (1) $\vec{B}=\nabla\times\vec{A}$. Also $a=a_0(T-T_c)/T_c$, where T_c is the upper superconducting transition temperature and $r_0=2e/\hbar c$. The London penetration depth $\lambda(T)$ is given by $\lambda^{-2}=4\pi p_0 r_0^2|\psi|^2$, $\alpha=\alpha_0(T-T_m')/T_m'$. The terms $\frac{1}{2}[\eta_1\vec{M}^2|\psi|^2+\eta_2|\nabla\vec{M}|^2]|\psi|^2$ express the effects of conduction-electron polarization and of spin-flip scattering on superconductivity.

The uniform superconducting state has the free-energy density

$$F_c=-a^2/4b \text{ for } T<T_c. \quad (2)$$

If $|\psi|\neq 0$, then $B=0$ in the bulk of the sample, and the question of magnetic order does not arise until $T<T_m'$. If, however, $|\psi|=0$, then $B=4\pi M$, and the free-energy density for the uniform magnetic state (with $H=0$) is

$$F_M=-(\alpha-4\pi)^2/4\beta, \quad T<T_m^0, \quad (3)$$

and

$$T_m^0=(1+4\pi/\alpha_0)T_m'. \quad (4)$$