Exciton-Exciton Interaction in $KMnF_3$

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Exciton dynamics in $KMnF_3$ at exciton densities up to 10^{16} cm^{-3} are examined with time-resolved emission spectroscopy. The exciton emission line shifts and broadens with increasing exciton density. A nonlinear exciton decay channel is observed. These effects are found to be consistent with an exciton-exciton process. The shift scales with the exciton density and suggests that the effect is dominated by pairwise interactions up to the densities reached in these experiments.

Interactions between Wannier excitons in semiconductors and between Frenkel excitons in organic van der Waals crystals have been extensively studied in recent years, but very little work has been done on interactions between Frenkel excitons in inorganic ionic compounds. Heretofore, the best evidence available for such interactions has been nonexponential fluorescence decay[1,2] and exciton-pair absorption spectra.[3] We present here observations of shifting and broadening of the exciton emission from $KMnF_3$ as a function of exciton density. These results are best explained by exciton-exciton interaction and supply the best evidence to date for the effect of energy renormalization at high density in a Frenkel exciton system.

Exciton dynamics were monitored by measurements of the intrinsic, purely electronic emission of the lowest $^4T_{1g}$ (I) exciton. In all Mn compounds the observed lifetime of this state is reduced several orders of magnitude from the radiative lifetime by nonradiative decay and fast transfer to impurity-induced acceptors.[4] The antiferromagnetic perovskite $KMnF_3$ was chosen for these experiments because the observed lifetime of ~8 ms at low excitation[5] is the longest reported for any stochiometric Mn compound, presumably because of less effective trapping. Even at low excitation levels (~10 mW cw unfocused) the ultimate exciton density obtained is limited by two-exciton decay rather than trapping or single-exciton decay.

The $^4T_{1g}$ state forms an exciton band and thus all transitions have to obey the $\Delta k = 0$ selection rule. An upper limit of 2 cm^{-1} can be set on the bandwidth[6] with the method used in Ref. 7. The degeneracy of the $^4T_{1g}$ state is partially lifted by spin-orbit interaction. Two weak magnetic dipole lines ($\Gamma_7 + \Gamma_8$ and Γ_8) are observed with an integrated absorption of ~0.06 cm^{-2} each and a splitting of 10 cm^{-1}. By convention they are labeled $E1$ and $E2$, respectively. We find the absorption line shape to be Gaussian to a distance of at least 2 standard deviations from the peak. The full width at half maximum (FWHM) varies from 3.5 cm^{-1} to 4.2 cm^{-1}, depending upon the origin of the sample. The measurements reported here were taken on the sample with the smallest FWHM since most of the linewidth is due to inhomogeneous broadening.

To investigate this system time-resolved emission spectra of the $E1$ transition were analyzed. This enabled us to determine both linewidth and peak position as a function of exciton density. In addition, decay measurements were made to verify that two-exciton decay is significant. Both data sets were taken simultaneously with a fast multichannel counter to record number of photons versus time at each step of a scanning spectrometer. The data were stored as a time×wave number matrix in a computer. This recording method allows one to reconstruct either a spectrum at any desired time delay or a decay curve at any desired wavelength. In addition, recording all the delayed spectra in a single scan eliminates any uncertainty in their relative calibration.

The samples were immersed in superfluid He for all measurements. Three different excitation techniques were employed. Steady-state spectra were measured with use of cw lasers at powers ranging from 0.1 to 2.5 W. Dynamic effects were observed with both a long-pulse and a short-pulse laser. A slow buildup of exciton density was provided by an acousto-optically modulated Ar laser (up to 2 W at 514.5 nm with pulses up to 10

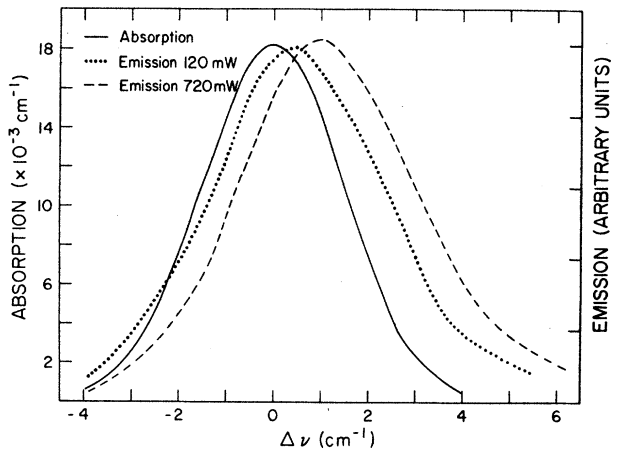

FIG. 1. Time-resolved emission spectra and exciton absorption line for different pump powers but the same gate (50 μs) and delay time (300 μs). Excitation is by 5-ms pulses at 514.5 nm. At higher pump powers, the exciton density buildup and the shift are more rapid. The curves depicted are the fits to the data after deconvolving the instrumental bandwidths.

ms in duration. Instantaneous buildup was obtained with use of 7-ns pulses from a frequency doubled Nd:YAlG (neodymium-doped yttrium aluminum garnet) laser (up to 150 mJ at 531.5 nm). All three methods used phonon-assisted transitions and thus populated the exciton band throughout the Brillouin zone. Because the purely electronic $E1$ transition is very weak much higher excitation levels are generated by pumping the phonon sideband.

We observed nonexponential exciton decay as well as redshifting and broadening of the $E1$ emission relative to the absorption line. The shift was 1.5 cm^{-1} and the linewidth 4.2 cm^{-1} (absorption 3.5 cm^{-1}) at a density of $\sim 10^{16}$ cm^{-3}. Both shift and broadening increased gradually during excitation by long pulses. At higher excitation the line shifted more rapidly just as the density built up faster (Fig. 1). Under high-intensity short-pulse excitation, the shift was immediate. The magnitude of the spectral effects increased and the decay became faster when decreasing the focus size while maintaining the same laser power or increasing the laser power while maintaining the same focus. These characteristic dependences upon excitation suggest that the effects are due to exciton-exciton interaction.

Before showing that all of these effects are completely consistent with the exciton-exciton interaction model, the possibility that they are due to local heating or nonequilibrium phonons produced by relaxation processes has to be considered. Spectral transfer, either within the inhomogeneous line or to impurity-induced acceptor states, is a phonon-assisted process and depends on the phonon population. Thus a time- and pump-dependent local temperature change could cause a line shift by population redistribution within the line or nonexponential decay by changing the rate of exciton transfer to impurity-induced acceptors. A sensitive probe of local temperature is provided by the ratio of $E2$ to $E1$ emission. The relaxation between these states has to be fast because no $E2$ emission is observed when pumping both levels by moderate cw excitation into the phonon sideband. Therefore the relative populations of these states are governed by a Boltzmann distribution and temperature changes as small as 0.3 K are detectable. No $E2$ emission was observed at the excitation levels used on these measurements, indicating that the effective local temperature was not increased above 2.2 K by the laser pulses.

The observed dependence on excitation cannot be explained by spectral transfer after ruling out local heating because only phonon assistance increases the transfer rates substantially. Furthermore, the one-phonon direct process, which would dominate the formation of an asymmetric population of the $E1$ density of states, is usually not observed for intraline transfer.[8] Another inconsistency with the spectral-transfer explanation is the observation that the line shift does not scale with the absorption linewidth. In equilibrium (i.e., cw excitation) the spectral transfer mechanism requires the emission to be proportional to the density of states (i.e., the absorption line) weighted with a Boltzmann factor. The shift is then

$$\Delta\nu = \delta^2/[(8\ln 2)k_B T],$$

where δ is the FWHM of the absorption line, k_B is Boltzmann's constant and T is the lattice temperature. The shift would be a quadratic function of absorption linewidth, but we found $\Delta\nu$ to be essentially the same under similar excitation for samples with δ in the range 3.5 to 4.2 cm^{-1}. We have to conclude that intraline spectral transfer cannot explain the observed effects and that it plays no significant role within the first few milliseconds, the time scale of our experiments.

Exciton-exciton interaction provides a simple and complete explanation for all spectral and temporal effects at the exciton densities reported. The significant quantity for the analysis is the exciton density $n(t)$. Its time dependence has to be

derived from the measured exciton emission intensity $I(t)$. $n(t)$ is well described by the lowest-order two-exciton decay induced by exciton-exciton interaction. The resulting rate equation in the absence of excitation is thus[2]

$$dn(t)/dt = -k_1 n(t) - k_2 n^2(t), \quad (1)$$

where k_1 and k_2 are the one- and two-exciton decay constants, respectively, averaged over the Brillouin zone. Because intraband relaxation of the excitons are fast compared with the time scale of our measurements[9] it is possible to replace sums of wave-vector–dependent rates with thermal averages. Solving (1) yields the time evolution of a given initial density $n(0)$,

$$n(t) = \frac{k_1}{k_2} \frac{n(0)}{[k_1/k_2 + n(0)]\exp[k_1 t - n(0)]}. \quad (2)$$

Although $n(t)$ is independent of the particular two-exciton processes involved, the relationship between $E1$ emission and $n(t)$ is not. To determine whether the nonlinear term in (1) contains a significant branching ratio for two-exciton decay with emission of an $E1$ photon, we measured the $E1$ emission intensity as a function of excitation power. No n^2 dependence was found. We also fitted the decay of the emission intensity $I(t)$ at several points in the line with the expression

$$I(t) \propto k_1 n(t) + (\gamma/\eta) k_2 n^2(t),$$

where γ is the two-exciton radiative ($E1$ photon) branching ratio and η the single-exciton radiative branching ratio. The best fits were obtained for γ either zero or very small. Consequently, the radiative two-exciton decay can be neglected and

$$n(t) \propto I(t). \quad (3)$$

Decay curves for initial exciton densities in the range 10^{13} cm^{-3} to 10^{16} cm^{-3} were fitted with (2). The densities were determined from fits to the rise of the $E1$ emission under long-pulse excitation by using the known absorbed photon flux. The rate constants obtained were $k_1 = (80 \pm 10)$ s^{-1} and $k_2 = (4 \pm 3) \times 10^{-11}$ cm^3 s^{-1}. The linear rate k_1 (radiative plus trapping) is much smaller than for MnF_2[2] ($k_1 = 8 \times 10^3$ s^{-1}) while the pair decay rate MnF_2: $k_2 = 5 \times 10^{-13}$ cm^3 s^{-1}) is larger. This suggests that $KMnF_3$ is the more suitable system for the study of exciton-exciton interaction.

Exciton-exciton interaction provides a complete explanation for the spectral effects. The relationship of the exciton density to the shift and broadening of the emission line agrees well with the theoretical predictions of a simple collision model developed for atomic spectra.[10] This approach has been used successfully to treat the interaction of Wannier excitons in Ge below the critical density for electron-hole–liquid formation.[11] The collision model is based on simplifying approximations. The excitons are assumed to be sufficiently dilute that collisions can be considered to occur only pairwise. This is verified by the fact that only single- and two-exciton terms are needed in (1) to describe completely the exciton decay. At the densities reached the mean interparticle spacing in our experiments is large, certainly larger than the range of any interaction mechanism. A further assumption is that the motion of the excitons is not diffusive between collisions. This agrees with our observation that the time behavior of the impurity-induced emission does not give any evidence for time-dependent (diffusion-limited[2]) spatial transfer. The model approximates the motion of the excitons by their classical trajectories. This does not impair any of the features observed in these experiments. Also excluded are instabilities of the crystal structure.

The details of the collision model have been worked out[10] and the results can be generalized for the $KMnF_3$ Frenkel exciton system. The total interaction energy is quadratic in exciton density while the energy change per exciton is linear. Therefore both the line broadening and line shift are linearly dependent on the exciton density. It is not possible to analyze the linewidths quantitatively since the emission line shape is not Gaussian and even at the highest densities reached most of the width is still inhomogeneous. Nonetheless the increase in linewidth scales roughly with the exciton density. The line shift $\Delta\nu$ can be measured and analyzed more accurately. The position of the exciton emission peak relative to the absorption peak is used as a measure of the line shift $\Delta\nu$ because the line shape is almost the same for all densities. Utilizing the above mentioned experimental technique, we determined $\Delta\nu$ as a function of $E1$ emission intensity for several excitation powers. Using (3) this gives the line shift as a function of exciton density n. Representative high– and low–excitation-level data sets are shown in Fig. 2. Both show clearly that the line shift is a linear function of exciton density as predicted by the collision model for a system of pairwise-interacting excitons.

The $\Delta\nu \sim n$ dependence is no longer exact at times later than a few milliseconds when the density of excitons bound at impurity-induced states reaches the same order of magnitude as the free-

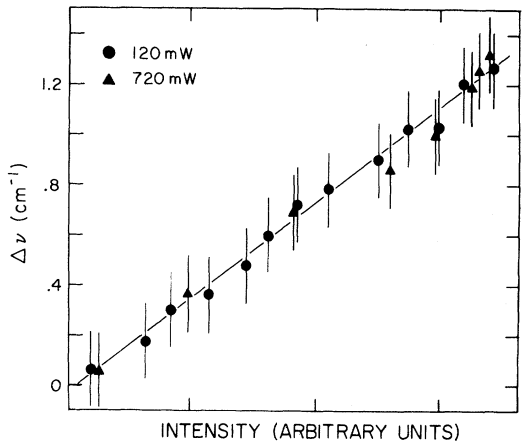

FIG. 2. Shift of the exciton emission peak as a function of integrated emission intensity. The shift $\Delta\nu$ is measured relative to the absorption peak. The emission intensity is proportional to the exciton density. The intensity units are the same (within the experimental error) for both excitation levels. The pump rate at 120 mW is $\approx 10^{21}$ cm^{-3} s^{-1}.

exciton density. These states have lifetimes longer than the $E1$ exciton and can accumulate large populations. We found experimental verification for the interaction of the free excitons with bound excitons. Therefore at later times the line shift $\Delta\nu$ depends on both the free-exciton density and the bound-exciton density. This effect is beyond the scope of this work and requires further investigation.

The exciton-exciton interaction mechanism cannot be concluded from the present experiments. In addition to multipolar and exchange interactions the excitons may interact via the strong a_{1g} and e_g strain fields associated with the $^4T_{1g}$ excitation in a cubic lattice. The change of the exciton energy by this lattice polarization is considerable, the tetragonal (Jahn-Teller) part alone lowers the energy by ~500 cm^{-1}.[6] Under these circumstances exciton interaction via the strain fields may be the dominant mechanism.

In summary, the $E1$ exciton state is significantly modified by exciton-exciton coupling. The interaction manifests itself as a shift and broadening of the exciton emission line and by nonexponential decay. These effects can be satisfactorily described by a simple collision model involving pairwise-interacting excitons.

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