Biexciton Decay in MnF_2

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Exciton dynamics in MnF_2 are investigated using time-resolved laser spectroscopy. At 1.7 K the decay of the intrinsic $E1$ exciton is nonexponential, independent of the particular traps present, and strongly dependent on pump intensity. We show that a biexciton decay model describes the qualitative behavior of the system and fits the decay data quantitatively over three decades. Values for the transfer rate to traps and the biexciton decay rate are also obtained.

We report the results of a direct investigation of exciton dynamics in the antiferromagnetic insulator MnF_2. The lowest $^4T_{1g}$ Mn state, designated as $E1$, is optically excited using a tunable-dye-laser system described elsewhere.[1] The subsequent exciton population is monitored by observing the very weak fluorescence originating from this intrinsic state. We show that the time evolution of the $E1$ exciton population at very low temperatures may be understood in terms of a biexciton decay model. Although similar behavior has been reported previously for large polarons in strongly coupled organic systems[2] and for essentially localized excited states of the shielded $4f$ electrons in $TbPO_4$,[3] this represents the first observation of biexciton decay in the case of a small polaron. Also in contrast to the well-studied organic materials where dipolar interactions predominate, MnF_2 is a magnetic insulator, and exchange is the dominant ion-ion interaction.

At 1.7 K, pulsed laser excitation of the $E1$ state results in a nonexponential decay that is independent of the particular traps present. In addition, there is a strong dependence on the pump intensity—the higher the intensity, the faster the decay at early times.

The possibility that the intensity dependence is due trivially to local heating produced by the laser pulse must be seriously considered, as we have observed a strong temperature dependence of the transfer rate to traps.[4] By pumping directly into the exciton band and into various parts of the phonon sideband, it is possible to create a constant initial exciton density while producing varying amounts of heating, and thus to isolate any purely thermal effects. The exciton decay at the same initial density appears to be independent of laser position within the absorption profile, indicating that any heating effects are negligible.

Diffusion-limited energy transfer, which is a common source of nonexponential behavior, could also be important in this system where the dispersion of the excited state is thought to be quite small.[5] An energy transfer process that is limited by the slow diffusion of the donor excitons results in a transfer rate that is time dependent, and manifests itself as a discrepancy between the feeding rate of the acceptor traps and the existing exciton population. A study of the energy transfer in samples doped with Zn, Er, or Eu in low concentration was undertaken to resolve this question.

Zn impurities are known to perturb the local field in such a way as to depress the excited-state energies on nearby Mn ions, thus creating traps for the intrinsic excitons.[6] The rare-earth ions themselves act as traps, and fluoresce at their own characteristic wavelengths. The feeding of the Mn and rare-earth traps, inferred from the time evolution of their fluorescence following pulsed excitation of the bulk Mn ions, is seen in all cases to track with the observed $E1$ decay during the first 200 μs. This indicates that the transfer rate does not change appreciably on this time scale, and consequently the radically nonexponential decay observed at these early times may not be attributed to diffusion-limited transfer.

It should be noted that we have not ruled out the possibility that energy transfer is diffusion limited in this system. The transfer rate may, indeed, undergo substantial change on a ms time scale, thus producing the gradual decrease in the exciton decay rate which occurs even at low pump intensity, and was first reported by Dietz, Meixner, and Guggenheim.[7]

The characteristics of the dependence on pump intensity indicate that the decay rate depends on the exciton population, namely

$$dN(t)/dt = -k(N)N(t),$$

resulting in a nonlinear rate equation. The simplest case, corresponding to

$$k(N) = k_1 + k_p N,$$

leads to a rate equation for the population given

by

$$dN(t)/dt = -k_1 N - k_p N^2. \quad (1)$$

The parameter k_1 represents the sum of all linear decay rates

$$k_1 = \frac{1}{\beta_r} + \sum_{\text{traps}} k_i , \quad (2)$$

where β_r is the radiative lifetime, (~ 33 ms), and k_i the transfer rate to a particular type of trap. k_p, on the other hand, must be interpreted as a decay rate due to the interactions of pairs of excitons.

The physical plausibility of such a formulation is indeed significant. The abundance of cooperative effects and two center transitions among the optical properties of MnF_2 is well known.[8,9] Of particular importance is the observation of exciton pair creation by the absorption of single UV photons in MnF_2.[10] Lines corresponding to $E2+E2$ (denoted as E_{22}) at 36 789 cm^{-1} and $E1+E2$ (denoted as E_{12}) at 36 917 cm^{-1} with energy shifts of -81 cm^{-1} and $+61$ cm^{-1}, respectively, from the combined single-exciton energies have been reported.[11] The large energy shifts indicate a sizable exciton-exciton interaction. No line corresponding to $E1+E1$ has been observed, and its absence has been attributed to the smaller exchange interaction expected for this transition. Because of the very long radiative lifetime of the single-exciton state, and the slow energy transfer to traps, however, the competing linear decay rate, k_1, is very small. As a result, a relatively small interaction between $E1$ excitons is adequate to account for the observed nonexponential and intensity-dependent behavior.

Our attempts to observe the radiative decay of bound exciton pairs as UV fluorescence have proved unsuccessful. This is not surprising, however, as it appears likely that the rate for an inverted cross relaxation would be much larger than the expected radiative decay rate. The end products for such a process would be one ion in the ground state, and the other in a higher excited state which would presumably decay nonradiatively to $E1$, resulting in no additional spectral features.

Qualitatively this biexciton decay model is completely consistent with the features of the $E1$ decay. It correctly predicts the intensity dependence, the nonexponential decay, and the lack of sensitivity to trap type or concentration. We consider now a quantitative comparison to the decay data. From Eq. (1) it is easily shown that the time derivative of the fluorescence intensity, $\dot{I}$, should satisfy the relationship

$$-\dot{I}/I = k_1 + k_p' I.$$

Consequently the ratio $-\dot{I}/I$ should be linear in I. This predicted linearity is used as a test of the theory. Note that the scale-dependent parameter, k_p, has been replaced by k_p', the two being related by $k_p N(0) = k_p' I(0)$.

In order to calculate I accurately, the decay data were fitted by computer to a smooth spline function constrained to generate a χ^2 value of zero. The splite function was subsequently differentiated, and the ratio $-\dot{I}/I$ plotted against I. Figure 1 shows such a plot for a nominally pure sample, with the error estimated from the uncertainty in the intensity data. The expected linearity is evident. A linear regression fit yields values for the parameters

$$k_1 = 7.9 \pm 0.4) \times 10^3 \ s^{-1},$$

$$k_p' = (6.5 \pm 0.5) \times 10^1 \ s^{-1}$$

$[k_p' I(0) \simeq 1 \times 10^6 \ s^{-1}]$. Recalling from Eq. (2) that k_1 is a sum of the radiative decay and transfer rates, and that $\beta_r \sim 33$ ms, this model predicts a net transfer rate to the traps of

$$k_1 \sim \sum_{\text{traps}} k_i \sim 8 \times 10^3 \ s^{-1}.$$

This is in good agreement with the observed ratio of trap to intrinsic fluorescence, which is estimated to be ~250,[12] and supports a net transfer rate of

$$\sum_{\text{traps}} k_i = \frac{I_{\text{traps}}}{I_{\text{intrinsic}}} \frac{1}{\beta_r} \sim (250) \frac{1}{33 \text{ ms}} \sim 7.6 \times 10^3 \ s^{-1}.$$

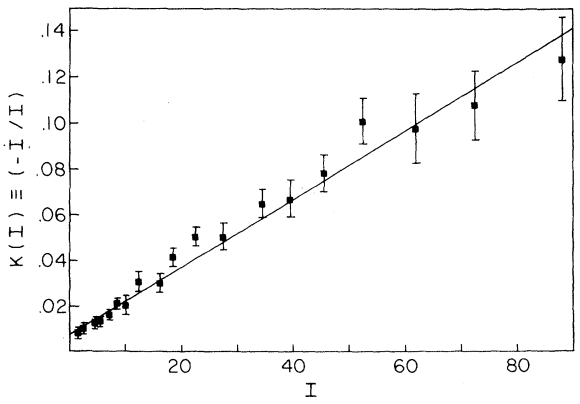

FIG. 1. The ratio $-\dot{I}/I$ against the intensity I. The linearity is used as a test of the biexciton decay model.

The initial exciton population, $N(0)$, is estimated from the laser power and absorption strength to be 6×10^{14} in an excited region of 3×10^{-4} cm^3, which yields a value for the pair decay rate per unit exciton density:

$$k_p = 5\times10^{-13}\ \text{cm}^3\ \text{s}^{-1}.$$

Using the $E1$ dispersion estimated by Dietz and Misetich[5] this corresponds to a classical cross section of $\sim10^{-13}$ cm^2, or a linear interaction of only 3–5 lattice spacings. Thus the exciton-exciton interaction need not be very strong or long range to account for the observed behavior. In fact, as expected, the pair decay rate observed in MnF_2 lies intermediate to the values reported for the strongly coupled organic systems and the weakly coupled $TbPO_4$.

The rate equation for the $E1$ population given in Eq. (1) may be solved analytically with the result

$$N(t) = \frac{k_1}{k_p}\frac{N(0)}{[k_1/k_p + N(0)]\exp(k_1 t) - N(0)},$$

with the corresponding equation for the intensity given by

$$I(t) = \frac{k_1}{k_p'}\frac{I(0)}{[k_1/k_p' + I(0)]\exp(k_1 t) - I(0)}.$$

As shown in Fig. 2, the resulting theoretical fit to the decay data is excellent over three orders of magnitude. The model predicts an asymptotic approach to purely exponential behavior with lifetime k_1^{-1}, which we do not observe, but as discussed earlier, the approximation that the transfer rate to traps is constant may not be valid on longer time scales.

We conclude that the puzzling aspects of the $E1$ decay behavior at very low temperatures are well described by this model in which interactions between pairs of excitons represent the dominant exciton decay mode at high exciton population densities. Note, however, that the necessary exciton-exciton interaction is not particularly large. It appears that the nonlinear effects are evident only because the radiative decay and transfer rates are so slow in this system. In fact, as the temperature is raised a few degrees the thermally activated transfer rate increases by three orders of magnitude and the nonlinear behavior is no longer evident.[4]

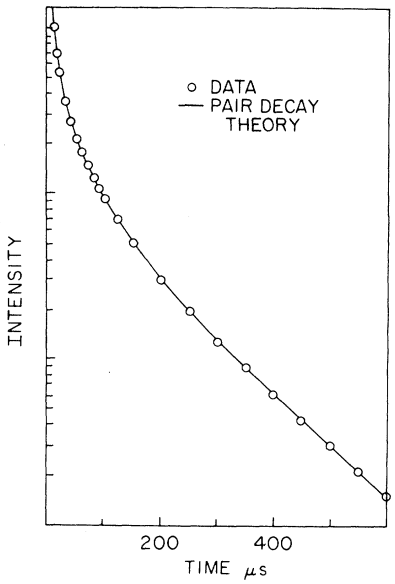

FIG. 2. Comparison of the theoretical curve predicted by the biexciton decay model and the $E1$ decay data taken at 1.7 K.

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