Fluorescence line narrowing of magnon sideband transitions in $MnF_2:Zn^{2+}$

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We report fluorescence line narrowing (FLN) studies of the magnon sideband of $^4T_1 \rightarrow {}^6A_1$ transitions in $MnF_2:Zn^{2+}$. We have successfully isolated magnon sideband profiles of near-resonant subsets of Mn^{2+} ions from within the inhomogeneously broadened line at Zn^{2+} concentrations up to 3%. Since the sideband profile mirrors the magnon density of states, this demonstrates the feasibility of using FLN to study local low-energy collective modes, such as spin waves, in highly disordered materials.

The effect of disorder on spin waves or other low-energy collective modes in crystals is of considerable interest. In the case of spin waves, the presence of nonmagnetic impurities randomly substituted for magnetic host ions upsets the long-range magnetic order, and leads to changes in the density of states. Neutron scattering studies in heavily Zn^{2+}-doped MnF_2, for example, have indicated a reduction in spin-wave peak energies.[1] Such experiments, however, are difficult to interpret, and yield only averages over all sites. Since the magnon sidebands accompanying pure electronic optical transitions reflect the spin-wave density of states, one might hope that a study of the sideband line shape in crystals of varying impurity concentration would provide a direct measure of changes in the magnon energy distribution. Unfortunately, the impurities also cause substantial inhomogeneous broadening of the electronic transitions,which when convoluted into the sideband profile tends to mask these changes. We report here the first use of fluorescence line narrowing (FLN) to isolate the magnon sideband profile from particular subsets of near-resonant sites within an inhomogeneously broadened level. We have observed narrowing in the sidebands up to an impurity concentration of 3% in Zn^{2+}-doped MnF_2, indicating the feasibility of using FLN to study local collective modes in highly disordered materials.

The samples used in this study were single crystals of MnF_2 of good optical quality with eight different Zn^{2+} concentrations ranging from 0.1% to 20%. The Zn^{2+} concentration was measured by neutron activation analysis and flame luminescence. The samples, which were immersed in liquid He at ~ 1.7 K, were excited with a 250-kW N_2 laser-pumped dye laser with a bandwidth ~ 1 cm^{-1}. The fluorescence was dispersed with a double monochromator and detected with a gated photon counting system.

Optical absorption into the Mn^{2+} band centered at $\sim 5\,200$ Å excites electrons into the $^4T_1$ manifold, of which only the lowest level $E1$ maintains a sizable population at low temperatures. Even in nominally pure samples the fluorescence from this level to the $^6A_1$ ground state is dominated by trap sites consisting of Mn^{2+} ions which are near neighbors of trace impurities, and whose energy levels are depressed below that of the intrinsic exciton state.[2] The spectra from these specific trap sites, as well as from the intrinsic state, consist of a direct electonic transition and magnon and phonon sidebands. The intrinsic spectrum may be isolated by gated detection at early times following pulsed excitation. In relatively pure samples, the direct $E1$ transition is quite narrow, < 1 cm^{-1}, allowing the magnon sideband profile to accurately mirror the spin-wave density of states.

As the Zn^{2+} concentration is increased, both the intrinsic and trap spectra broaden.[3] A series of trap spectra at various Zn^{2+} concentrations is shown in Fig. 1. The inhomogeneous broadening of the direct transition masks any simultaneous changes that might be occurring in the magnon energies, since the sideband line shape is a convolution of the two distributions. In order to eliminate the contribution from the inhomogeneous broadening of the direct transition, we have excited only a

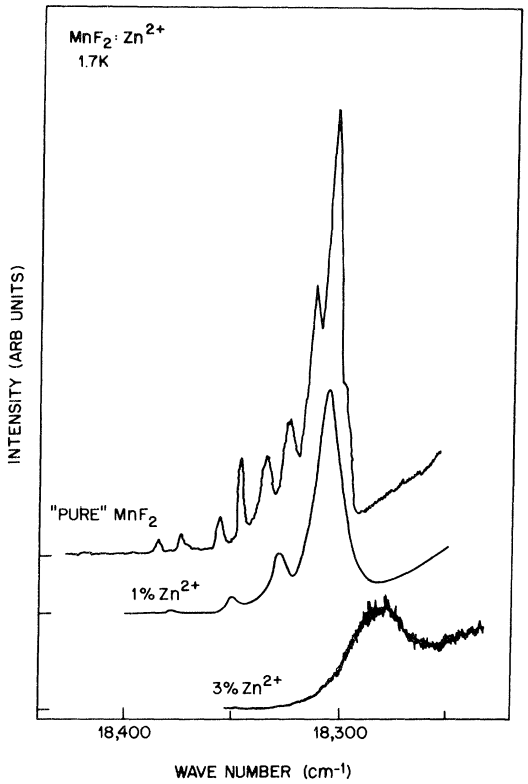

FIG. 1. Trap fluorescence spectra at various Zn^{2+} concentrations.

narrow subset of the Mn^{2+} ions using the 1-cm^{-1} bandwidth laser. This allows the observation of fluorescence from this near-resonant set of ions, provided that the signal is detected prior to any substantial nonresonant energy transfer. We have used this technique, known as FLN, to study both the intrinsic and trap transitions.

The intrinsic $E1$ line broadens quickly with Zn^{2+} concentration, reaching ~ 10 cm^{-1} by only 1.0%, thus reducing even further the already weak absorption in any given 1-cm^{-1} window. Nevertheless, by pumping within the inhomogeneously broadened $E1$ profile, we have observed narrowing in the intrinsic magnon sideband σ_1^* up to 1.5% Zn^{2+}. Figure 2 shows a set of narrowed spectra detected with a 40-μs gate at 1-μs delay, indicating that the excitation has remained primarily on the near-resonant Mn^{2+} ions during this time. Excitation into the broad phonon sideband, which produces no site selection, results in a σ_1^* line shape that is a broad envelope of these narrowed profiles. At this low concentration, the sideband line shapes indicate no changes in the magnon distribution, in agreement with the neutron scattering results.[1] Owing to the extreme weakness of the signal, this

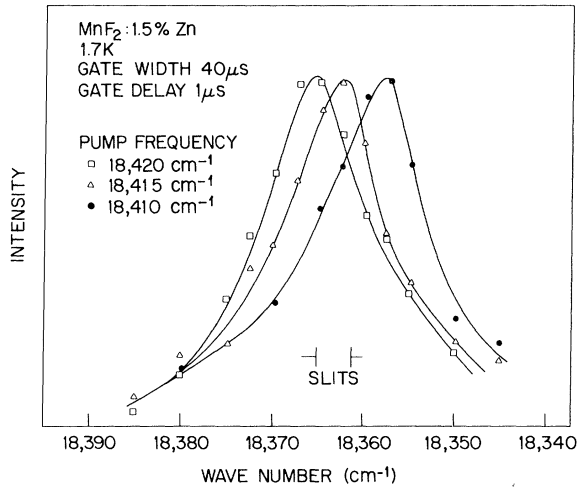

FIG. 2. Fluorescence line narrowed profiles of the intrinsic magnon sideband σ_1^*.

investigation of the intrinsic transition could not be extended to higher Zn^{2+} concentrations using the laser power available.

At somewhat higher concentrations, we have been able to take advantage of the increasing number of Mn^{2+} ions that are nearest neighbors (NN) of Zn^{2+} impurities, and excite these traps directly. This is not feasible at low concentrations where the number of such sites is too small, and the excitation spectrum of the second NN magnon sideband fluorescence shows only the intrinsic absorption structure. At a concentration of a few percent Zn^{2+}, an additional line appears in the excitation spectrum, presumably the magnon sideband absorption of the trap itself. This line is quite broad, however, since at these concentrations, a second NN of a particular Zn^{2+} is also likely to be a fifth or sixth NN of another Zn^{2+}. In other words, the trap level contains considerable inhomogeneous broadening. Again, by exciting with a 1-cm^{-1} laser we have observed narrowing in the magnon sideband fluorescence of the second NN trap. Note that by exciting in the magnon sideband, we are increasing our effective laser bandwidth to span the sideband linewidth, an additional ~ 10 cm^{-1}. Shown in Fig. 3 is a set of narrowed profiles obtained in this manner, as well as the full inhomogeneously broadened spectrum from all second NN sites excited by pumping in the phonon sideband region.

It is clear that even taking into account the additional bandwidth due to excitation in the magnon sideband, the narrowing is less effective for the trap transition than observed in the intrinsic transition.

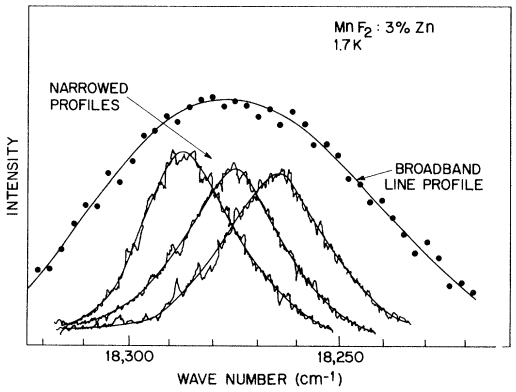

FIG. 3. Trap fluorescence line narrowing of the magnon sideband from the second NN of Zn^{2+} impurities. The narrowed and broadband profiles are excited by pumping into the magnon and phonon sidebands of the trap, respectively.

Since energy transfer among localized trap states is probably even less favorable than nonresonant transfer within the intrinsic band, it is more likely that there is an alternate cause of the broadening, such as accidental degeneracy of the absorption energy at different sites. In fact, at 5% Zn^{2+}, we see very little narrowing at all, and the excitation spectrum of the second NN fluorescence no longer shows any structure. This indicates a complete overlap of direct transitions from some sites with magnon and phonon transitions from others. Such simultaneous absorption by sites with differing $E1$-level energies precludes the use of FLN at higher concentrations in this system.

In summary, we have observed fluorescence line narrowing of the magnon sideband profile in the intrinsic and trap $^4T_1 \rightarrow {}^6A_1$ transitions in MnF_2:Zn^{2+}. The available laser power limited observations of the intrinsic sideband to Zn^{2+} concentrations of 1.5%. On the other hand, the accidental degeneracy problems occurring in the study of the trap fluorescence above $\sim$ 3% is inherent to the MnF_2 system, and would presumably also affect the study of the intrinsic transition. The very large inhomogeneous widths result in overlap of direct and phonon- and magnon-assisted transitions from sites with different $E1$ energies, effectively ruling out the use of the FLN technique at higher concentrations. Nevertheless, the successful narrowing of assisted transitions attained in this study indicates the general feasibility of using FLN to study local magnon modes or other low-energy collective modes in highly disordered materials.

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*Work performed while at University of Wisconsin, Madison, Wisconsin.

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