

Fluorescence Studies of the $Mn^{2+} \rightarrow Er^{3+}$ Energy Transfer in MnF_2

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The antiferromagnetic crystal MnF_2 presents a fluorescence band which peaks at $\sim 6300 \text{ \AA}$ and is $\sim 600\text{-\AA}$ wide at 77 K and peaks at $\sim 5820 \text{ \AA}$ and is $\sim 525\text{-\AA}$ wide at 4.2 K . Going down in temperature, the fluorescence shows a sharp increase at $\sim T_N/2$ ($T_N = 67 \text{ K}$ Néel temperature). This fluorescence is due to localized traps which reside below the Mn absorption edge; in contrast, the absorption spectrum is due to exciton-type processes in which the energy is delocalized and moves freely throughout the crystal. When Er impurities are present three additional groups of fluorescence lines located at ~ 6710 , ~ 9760 , and $\sim 15300 \text{ \AA}$ are observed and were assigned by us to transitions from the ${}^4F_{9/2}$, ${}^4I_{11/2}$, and ${}^4I_{13/2}$ levels to the ${}^4I_{15/2}$ level of Er^{3+} , respectively. The excitation spectrum of each transition reveals that most of the Er excitation energy is due to $Mn \rightarrow Er$ energy transfer; this process was found to be of the nonradiative type and to be more efficient at ~ 77 than at 4.2 K . Both the thermal dependence of the fluorescence and that of the energy transfer are explained as due to the emptying of the higher Mn trap into the lower Mn excitonic band.

I. INTRODUCTION

The fluorescent crystal MnF_2 has been the object of spectroscopic investigations, primarily because of the interest in the possible effects of the antiferromagnetic ordering which occurs at $\sim 67 \text{ K}$. In particular, Holloway *et al.*¹ first reported an anomalous broadband fluorescence shift in the MnF_2 fluorescence and subsequently related this anomaly to a temperature dependence of the excited-state exchange interaction.² In addition to MnF_2 they found similar fluorescence behavior in $KMnF_3$, $RbMnF_3$, $NaMnF_3$, and $CsMnF_3$, all of which become magnetically ordered at low temperatures.

Later work³ on MnF_2 dealt with the investigation of the sharp fluorescence lines residing at the high-energy side of the broadband fluorescence. These sharp lines were identified as due to pure electronic transitions and associated magnon sidebands. The origin of these electronic lines was attributed to nonequivalent impurity-perturbed Mn^{2+} ions which acted as traps. The thermal dependence of these lines was explained in terms of an activation energy "boil-off" process from these local excitation states into the intrinsic exciton levels characteristic of the Mn^{2+} absorption. The broadband fluorescence was interpreted to be of vibronic nature and to have as no-phonon line either the pure electronic transition or the stronger magnon sideband.

The energy transfer from Mn^{2+} to rare-earth ions in the antiferromagnetic crystals MnF_2 and $RbMnF_3$ has also been the object of several investigations.⁴⁻⁷ The rare-earth ions in the cases studied were Eu^{3+} and Nd^{3+} . In the present study we report the observation of a nonradiative energy transfer process from Mn^{2+} to Er^{3+} . Further, we

present a model which explains the thermal dependence of the $Mn \rightarrow Er$ energy transfer in terms of the thermal dependence of the Mn^{2+} excitations.

II. EXPERIMENTAL

The following samples were used in the present study: (a) a crystal MnF_2 of dimensions $5 \times 2 \times 2$ mm obtained from Dr. A. Linz of MIT and (b) a crystal $MnF_2:Er$ (1 mole%) of dimensions $\sim 4 \times 3 \times 2$ mm obtained from Semi-Elements Inc.

The fluorescence spectra were obtained by exciting the sample with the light from a Sylvania model No. DVY 650-W tungsten source, filtered through a $CuSO_4$ solution which has a bandpass, $3500\text{--}5500 \text{ \AA}$. The fluorescence was observed at 90° to the direction of excitation, chopped and focused onto the entrance slit of a model No. 213 McPherson 1-m scanning monochromator which has a dispersion of 15 \AA/mm . When observing the fluorescence in the optical region the signal was detected by either a RCA 7102(S-1) or 7265(S-20) photomultiplier and amplified by a PAR 122 lock-in amplifier; the 7102 photomultiplier was cooled by crushed dry ice. When observing the fluorescence in the infrared region, a lead sulfide detector and a built-in preamplifier replaced the photomultiplier. When monitoring the Er^{3+} transitions ${}^4I_{11/2} \rightarrow {}^4I_{15/2}$ ($\sim 9760 \text{ \AA}$), ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ ($\sim 6710 \text{ \AA}$), and ${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ ($\sim 1.53 \text{ \mu m}$) the following filters were used between the sample and the monochromator: Corning model No. 2-64, Corning model No. 3-69 (both sharp cutoff), and a 1-\mu m silicon low pass, respectively.

The excitation measurements were performed by selectively pumping the sample by means of a model No. 82-410 Jarrell-Ash monochromator and detecting the fluorescence output through proper interference filters. A Sylvania model No. DVY

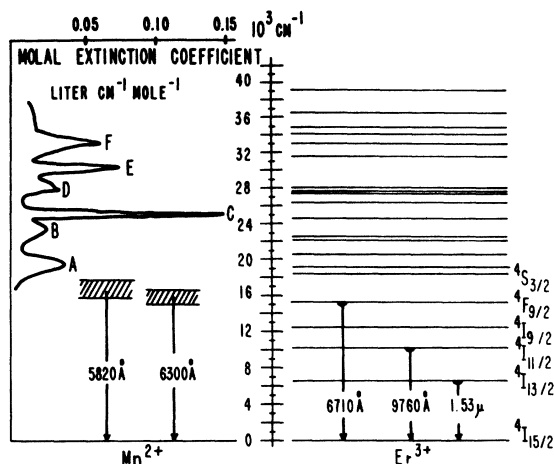


FIG. 1. Energy-level schemes of Mn²⁺ and Er³⁺ in MnF₂:Er.

650-W lamp was used as the exciting source.

The measurements of fluorescence response to pulsed excitation were performed by using model No. FX-12 or FX-33 EG & G flash tubes, monitoring the fluorescence through proper interference filters and detecting the signal by means of a photomultiplier (RCA model No. 7102 or 7265) or a lead-sulfide detector. The fluorescence signal was observed and photographed on a Tektronix model No. 533 oscilloscope.

For measurements at room temperature and

below, the sample was mounted in a Janis model No. 8 DT cryostat. The sample temperature was varied by using an exchange-gas technique.

III. EXPERIMENTAL RESULTS

A. Absorption, Fluorescence, and Excitation Spectra

The energy-level schemes of Mn²⁺ and Er³⁺ in MnF₂ are presented in Fig. 1 as derived from absorption, fluorescence, and excitation measurements. The absorption data were derived from a spectrum we ran using a Cary model No. 14 absorption spectrophotometer and from Refs. 8 and 9; for convenience the absorption bands are labeled A, B, C, etc.

The fluorescence spectrum of Mn²⁺ in MnF₂ was measured for temperatures ranging from 4.2 to 110 °K. The fluorescence emission peaks at ~6300 Å and is ~600 Å wide at 77 °K, and peaks at ~5820 Å and is ~525 Å wide at 4.2 °K. As the temperature decreases, the Mn fluorescence shows a sharp increase at ~½T_N, consistent with some previous data.² Above 110 °K no Mn²⁺ fluorescence is observed. Sharp lines appear on the short-wavelength side of the fluorescence band at low temperature; their positions and relative intensities resemble closely those observed by Greene *et al.*³

The Mn²⁺ fluorescence in MnF₂:Er is weaker than that of the pure sample but exhibits the same general behavior; no Mn²⁺ fluorescence is observed under continuous excitation at and above 77 °K in

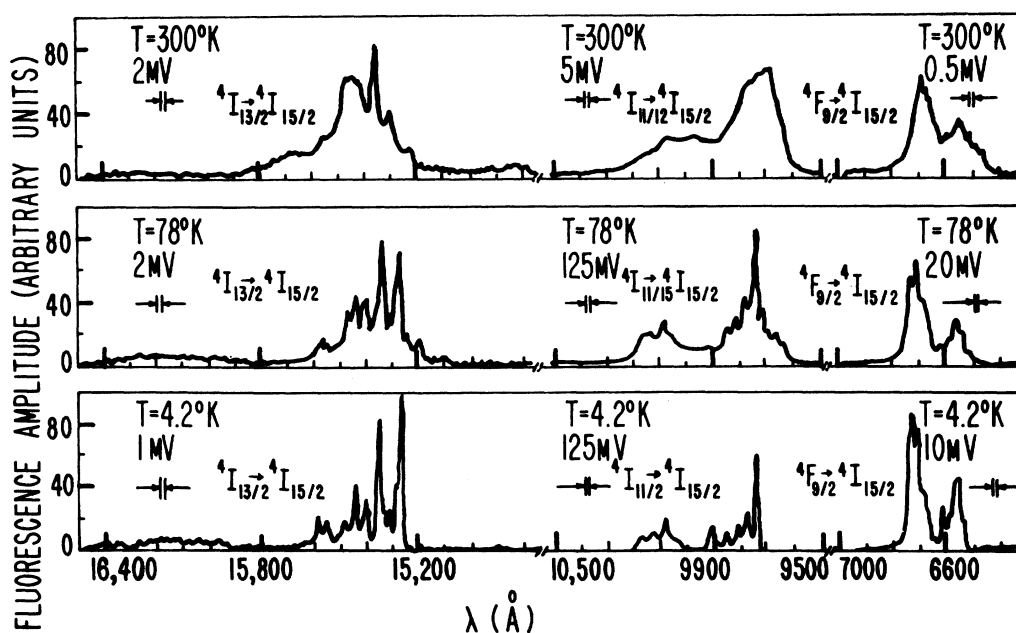


FIG. 2. Fluorescence spectrum of Er³⁺ in MnF₂:Er. The input and output slits of the McPherson model No. 213 monochromator were set at 700 μm for all measurements. The mV indicate the sensitivity scale of the lock-in amplifier.

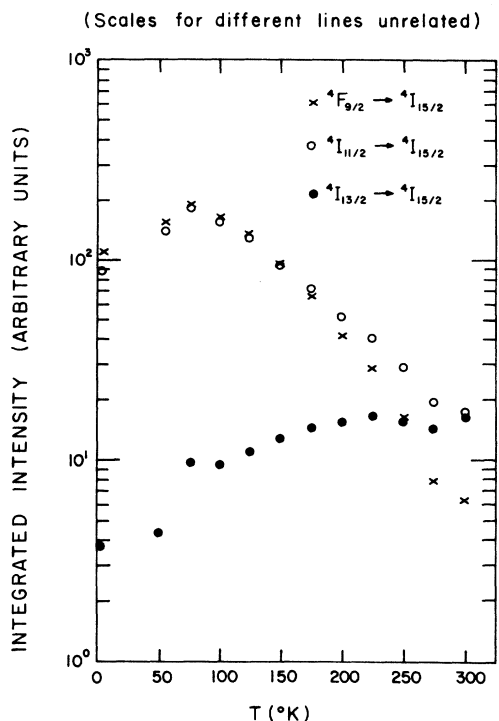


FIG. 3. Thermal dependence of the Er^{3+} fluorescence intensity in $\text{MnF}_2:\text{Er}$.

this sample.

The fluorescence spectrum of Er^{3+} in MnF_2 is presented in Fig. 2 for temperatures 4.2, 78, and 300 °K. The spectrum consists of three groups of lines centered at 6710 Å, 9760 Å, and 1.53 μm which we assigned to transitions from the ${}^4F_{9/2}$,

${}^4I_{11/2}$, and ${}^4I_{13/2}$ levels to the ${}^4I_{15/2}$ ground level, respectively.¹⁰ In what follows we shall refer to these three groups of lines either as to the three "lines" at 6710 Å, 9760 Å, and 1.53 μm , or to the ${}^4F_{9/2}$, ${}^4I_{11/2}$, and ${}^4I_{13/2}$ "fluorescence."

We measured the thermal dependence of the integrated intensity of each of the three Er lines; the results of these measurements are reported in Fig. 3. As the temperature is raised from 4.2 to 77 °K, the integrated intensity of all three Er lines increases; the increase factor is 1.7, 2.0, and 2.6 for the fluorescence originating at the ${}^4F_{9/2}$, ${}^4I_{11/2}$, and ${}^4I_{13/2}$ levels, respectively. Going from 77 to 300 °K, the integrated intensity of the ${}^4F_{9/2}$ fluorescence decreases by a factor of 30, the integrated intensity of the ${}^4I_{11/2}$ fluorescence decreases by a factor of 10.6, and the integrated intensity of the ${}^4I_{13/2}$ fluorescence increases by a factor of 1.7. These measurements were made by optically exciting the sample through a CuSO_4 filter (bandpass 3500–5200 Å) resulting in the pumping of the system through the excitation bands above the ${}^4F_{9/2}$ level.

The excitation spectrum of the Mn fluorescence in MnF_2 is reported in Fig. 4. This spectrum was obtained by monitoring the Mn fluorescence at 6300 Å when varying the wavelength of the pumping light through the absorption spectrum. The excitation spectra correlate well with the Mn absorption spectra and are labeled accordingly. The same spectrum (except for different intensity scales) was obtained when monitoring the Mn fluorescence at ~ 5800 Å.

The excitation spectra of each of the three Er

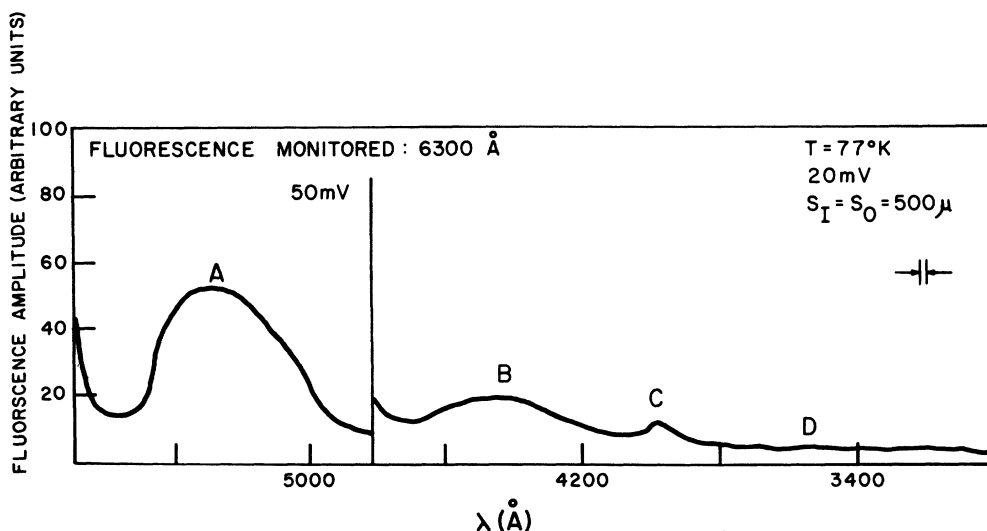


FIG. 4. Excitation spectrum of Mn^{2+} in MnF_2 . S_I and S_0 indicate the widths of the input and output slits, respectively, of the Jarrell Ash model No. 82-410 monochromator.

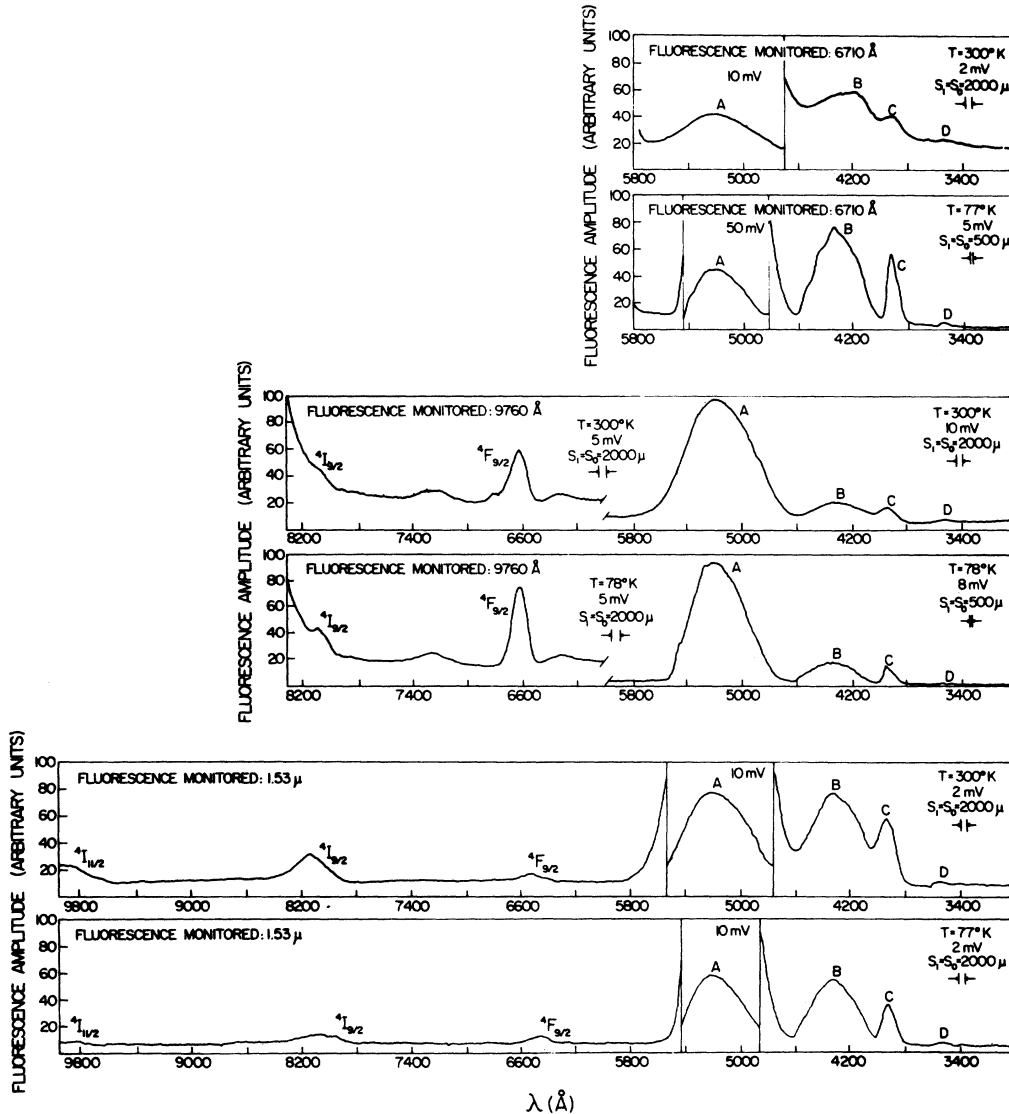


FIG. 5. Excitation spectra of Er^{3+} in $MnF_2:Er$.

transitions at 77 and 300 °K are presented in Fig. 5. The Mn absorption bands A, B, C, and D appear in each excitation spectrum at both temperatures.

B. Fluorescence Response to Pulsed Excitation

We measured the decay pattern of the Mn emission at 5820 and 6300 Å by subjecting the samples to pulsed optical excitation. The results of these measurements for the $MnF_2:Er$ sample are reported in Fig. 6; the lifetime at 5820 Å is 33 msec at 4.2 °K, 30 msec at 27 °K, and decreases abruptly at ~30 °K, the same temperature at which the shift in the peak of the Mn fluorescence occurs. The lifetime at 6300 Å is 30 msec at 4.2 °K, 28 msec at 30 °K, and 24 msec at 48 °K, decreases abruptly to a value of 5.8 msec at 68 °K, and continues to decrease smoothly at higher tempera-

tures. It should be noted that the lifetimes at 5820 and 6300 Å differ in the temperature region 4.2–40 °K.

The lifetimes of the Mn fluorescence at the same two wavelengths in the MnF_2 sample are similar to those of the $MnF_2:Er$ sample, except that the low-temperature lifetimes are a few milliseconds longer for both wavelengths and the lifetime at 5820 Å shows a somewhat more abrupt decrease at ~30 °K.

We measured also the decay patterns of the three Er lines in MnF_2 ; the experimental results are reported in Fig. 7. The lifetimes of the ${}^4F_{9/2}$, ${}^4I_{11/2}$, and ${}^4I_{13/2}$ levels at 4.2 °K are 280 μsec, 10 msec, and 22 msec, at 77 °K are 245 μsec, 9.2 msec, and 17 msec, and reduce at 300 °K to 128

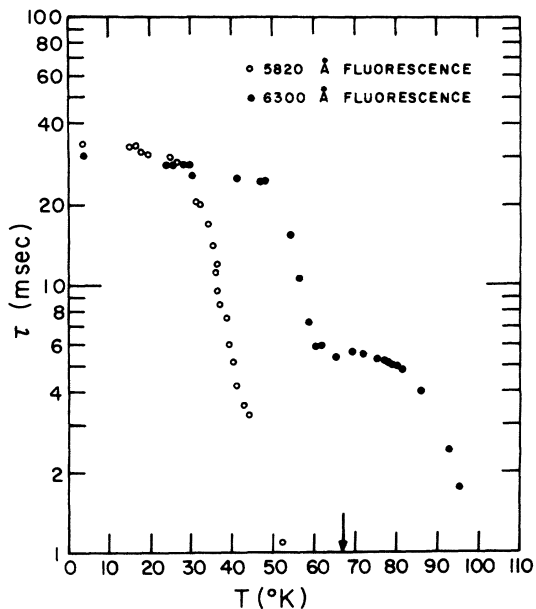


FIG. 6. Lifetimes of Mn^{2+} in $\text{MnF}_2:\text{Er}$. The arrow is at $T = T_N$.

μsec , 6.2 msec, and 15.7 msec, respectively. The decay pattern of the ${}^4F_{9/2}$ level is essentially exponential with a deviation to longer time constants at the end of the decay. The decay patterns of the lower two levels present a fluorescence rise at the end of the pulse followed by an exponential decay; the lifetimes shown in Fig. 7 for these two levels represent the time constants of the exponential decays.

IV. INTERPRETATION OF RESULTS

A. Mn^{2+} Fluorescence Characteristics

The structure and thermal dependence of the Mn^{2+} fluorescence have been examined by past workers.^{1-3,11} The Mn^{2+} fluorescence at very low temperatures consists of a number of sharp lines, due to the presence of several impurity-perturbed Mn^{2+} excited levels and of an accompanying broadband, considered to be due to phonon-assisted transitions.^{3,11} The sharp lines residing at the high-energy side of the broadband fluorescence are present only at low temperatures and disappear following "activation-type" processes, which produce a thermal dependence of their lifetimes of the type³

$$\tau_F^{-1} = p_0 + p_1 e^{-\Delta E/kT}. \quad (1)$$

The broadband emission consists of several overlapping phonon sidebands which, because of the great number of no-phonon lines, may be difficult to isolate.

The following observations, which are in agree-

ment with this model, can be derived from our measurements:

(i) The excitation measurements of the Mn^{2+} fluorescence band give the same spectra regardless of the wavelength monitored and show therefore that all the Mn^{2+} ions are excited via the same absorption bands.

(ii) We have isolated two distinct decay patterns for the Mn^{2+} fluorescence at 5820 and 6300 Å. In particular, we have extended the measurements of the lifetimes of the 6300-Å fluorescence done by Holloway *et al.*² below 40°K and shown that the fluorescence lifetimes at 5820 and 6300 Å below this temperature are different. This result confirms the fact that there are at least two corresponding superimposed bands originating from two distinct levels.

(iii) The study of the thermal dependence of the lifetimes at 5820 and 6300 Å confirms the existence of activation-type processes. We studied in detail the temperature dependence of the fluorescence lifetime at 5820 Å and fitted this dependence with a curve of the type (1). The results of this fitting are shown in Fig. 8. We found $p_1 = 4 \times 10^7$ and 10^6 sec^{-1} for MnF_2 and $\text{MnF}_2:\text{Er}$, respectively; for both $\Delta E = 250 \text{ cm}^{-1}$, and p_0 equal to inverse of the fluorescence lifetime at very low temperatures. This difference in energy ΔE corresponds approximately to the energy separation between the lower edge of the absorption A band of Mn and the upper edge of the 5820-Å fluorescence band. Goen *et al.*⁷ observed a similar effect for Mn^{2+} in RbMnF_3 and postulated the existence of a thermalized condition between the 5820-Å band and the

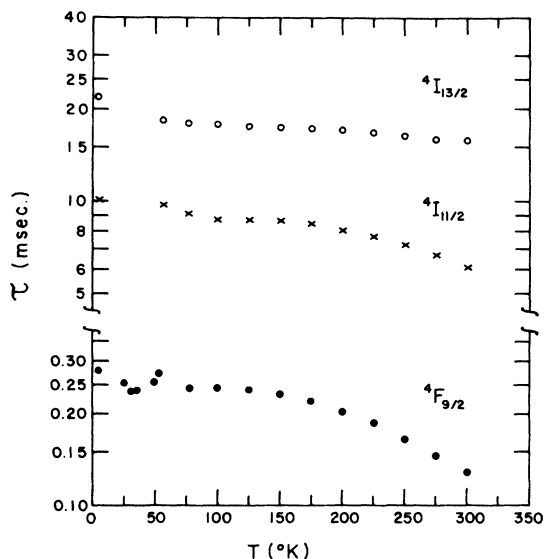


FIG. 7. Lifetimes of the Er^{3+} metastable states in $\text{MnF}_2:\text{Er}$.

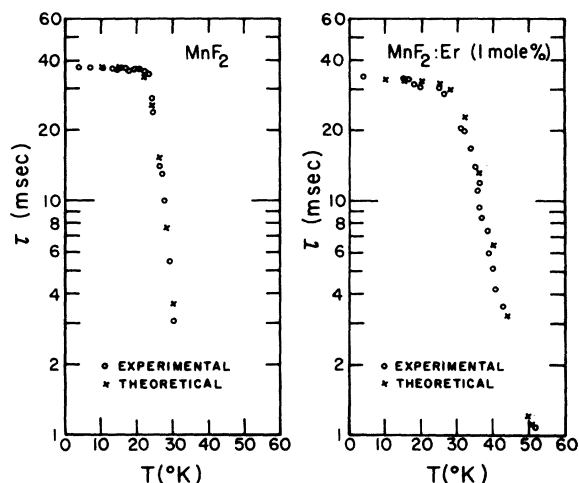


FIG. 8. Theoretical fitting of the Mn²⁺ lifetime at 5820 Å.

A band of Mn²⁺. In any case, thermalization may not necessarily be present; however, Eq. (1) implies the existence of an activation-type process whereby the level responsible for the 5820-Å fluorescence empties itself into the upper A band of Mn²⁺. A similar attempt was made to fit the thermal dependence of the lifetime at 6300 Å; this lifetime, as seen in Fig. 6, decreases considerably at ~50 °K and again at the higher temperature ~85 °K. The general shape of the curve suggests two activation processes taking place at the two temperatures above. [Indeed it was possible to perform reasonable fittings of the first portion of the curve (4.2–60 °K) and of the second portion of the curve (65–100 °K) with formula (1).] These results indicate that the 6300-Å fluorescence band may be due to two, rather than one, fluorescent levels; we feel, however, that no definite conclusion may be derived in this regard.

(iv) Finally, the Mn²⁺ fluorescence shows the same structural and thermal behavior in the nominally pure and Er-doped samples.

B. Er³⁺ Fluorescence Characteristics

The Er³⁺ transitions responsible for the fluorescence of this ion are represented in Fig. 1. These assignments were made by using (a) the energy-level diagram of Er³⁺ in Fig. 1, derived from Dieke¹² and (b) the information derived by selectively exciting the various Er³⁺ levels.

We examined in detail the radiative and radiationless processes of Er³⁺ in MnF₂.¹⁰ The thermal dependence of the three fluorescence lines and of the respective lifetimes revealed a mode of relaxation for the Er³⁺ ion, whereby a fluorescent level is excited only by nonradiative multiphonon decay of the next higher level.

Since no fluorescence is observed from the Er levels higher in energy than the ⁴F_{9/2} level, every initial excitation of these levels results in the excitation of the ⁴F_{9/2} level. Under these conditions of stepwise relaxation, if the sample were optically pumped only into the Er levels above ⁴F_{9/2}, the intensity of the ⁴F_{9/2} fluorescence and the ⁴F_{9/2} lifetime should present the same thermal dependence. We observed experimentally that from 4.2 to 77 °K this fluorescence increases by a factor of 1.7 while the lifetime decreases by a factor of 1.14; from 77 to 300 °K the fluorescence decreases by ~30 and the lifetime decreases only by a factor of 1.9. We explain the difference in the thermal dependence of the ⁴F_{9/2} fluorescence and lifetime as due to the fact that the Er system is also excited via the Mn absorption bands; this excitation is found to increase from 4.2 to 77 °K and to decrease from 77 to 300 °K.

C. Mn → Er Energy Transfer

The experimental evidence of the Mn → Er energy transfer is given by the Er³⁺ excitation spectra in Fig. 5. In these spectra the Er absorption bands are also present but most of the Er excitation energy is a result of the Mn → Er transfer.

Information about this energy transfer process can also be derived from fluorescence intensity measurements. The three Er lines (see Fig. 3) increase in intensity from 4.2 to 77 °K. Under the same temperature change, the intensity of the Mn emission in both samples MnF₂ and MnF₂:Er was seen to decrease; this is contrary to the behavior expected for a radiative transfer from Mn to Er. Also the fact that even when no Mn fluorescence is detectable (say, at room temperature) in both samples, Mn → Er energy transfer is still present in the doped sample as is shown by the excitation spectra. This is an additional proof of the non-radiative nature of the transfer.

Consider now the excitation spectrum of the 9760-Å line (Fig. 5); the contribution of the Mn bands substantially decreases with respect to that of the Er bands when the temperature is raised from 77 to 300 °K. (Note the smaller slit widths used on the monochromator through which the exciting light is passed for the Mn bands at the lower temperature.) This indicates that the transfer process is more efficient at 77 than at 300 °K. On the basis of this result and of the considerations made at the end of Sec. IV B, we can say that the efficiency of the Mn → Er energy transfer process increases from 4.2 to 77 °K and then decreases from 77 to 300 °K.

We have already ascertained the fact that the Mn → Er energy transfer process is of nonradiative nature. When such processes occur it is expected that the lifetime of the sensitizer in the presence

of the activator is shorter than the lifetime of the sensitizer when alone; in the present case the decay pattern of the Mn fluorescence is the same in absence or in the presence of the Er activator. On the other hand, we have established the fact that the level associated with the 5820-Å fluorescence in both MnF_2 and $\text{MnF}_2:\text{Er}$ depletes itself thermally into the lowest Mn absorption band. In particular, the temperature region in which this depletion occurs is the region in which the $^4F_{9/2}$ fluorescence of Er (whose intensity reflects the efficiency of the energy transfer) shows an increase. This last consideration suggests the hypothesis that the energy transfer process is taking place between the Mn bands and the resonant Er levels and that the increase in the efficiency of the transfer from 4.2 to 77 °K is due to the increased energy available in the A band of Mn. Moreover, the absence of direct interaction between the levels responsible for the Mn broad fluorescence and the Er levels points to the conclusion that these Mn levels are localized. This conclusion does not contradict the hypothesis that the broad fluorescence is of vibronic nature and has as zero phonon lines the sharp lines due to the localized excitons.

V. CONCLUSIONS

The established model for the temperature dependence of the Mn^{2+} fluorescence³ can now be extended to include the Mn → Er energy transfer. The Mn band emission originates from at least two real metastable levels which are the result of non-equivalent localized traps. Both of these traps are excited via the Mn absorption bands. Because of the high concentration of Mn and the relatively strong interaction between the Mn ions in MnF_2 , the optical absorption may be expected to be an

exciton-type process, in which the excitation energy is delocalized and moves freely throughout the crystal. As the temperature is increased from 4.2 °K, the trap responsible for the 5820-Å fluorescence, being energetically closer to the first absorption band, becomes thermally quenched. This quenching provides an increase in the amount of excitation of the lowest Mn absorption band. Considering the energy-level scheme we can see that there are several Er levels which are energetically in resonance with the Mn absorption bands. We may assume that the Mn → Er energy transfer takes place via these resonances. The observed thermal dependence in the energy transfer process is explained in terms of the amount of excitation energy present in the Mn A band. Specifically, at very low temperatures, the excitons are relatively free to move throughout the lattice except for their interaction with defects and the Er impurities. The number of excitons maintained in the A band actually increases as the temperature is raised above 4.2 °K, since this band is replenished by the thermal quenching of the higher Mn fluorescence trap; this allows a greater number of excitons to interact with Er. As the temperature is raised above 77 °K, exciton-phonon interactions become increasingly competitive with the impurity interaction; this results in a decreasing amount of energy transferred to Er as the temperature is further raised.

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