PHYSICAL REVIEW B VOLUME 28, NUMBER 5 1 SEPTEMBER 1983

Energy transfer and luminescence in $RbMn_xMg_{1-x}F_3$

J. Danko, D. Pacheco, and B. DiBartolo
Department of Physics, Boston College, Chestnut Hill, Massachusetts 02167

(Received 28 February 1983)

An investigation, directed toward an understanding of the concentration-dependent characteristics of Mn-Mn energy transfer, has been carried out in $RbMn_xMg_{1-x}F_3$ via a detailed luminescence study from 4 to 120 K. The emission of $RbMn_xMg_{1-x}F_3$ down to a 40 at. % Mn^{2+} concentration consists of two distinct Mn^{2+} bands which are featureless except in the case of the stoichiometric system. The bands are attributed to two localized traps positioned below the lowest excited level of Mn^{2+}. The variation of the spectra and of the decay patterns with temperature indicate a "boil-off" mode of decay for the shallower trap and nonradiative decay to the ground state for the deeper trap. The details of the kinetics have allowed us to calculate the rate of energy transfer to the shallower luminescence trap for the various samples. It can be concluded that an efficient non-diffusion-limited transfer of excitation exists in $RbMn_xMg_{1-x}F_3$ down to at least a 40 at. % Mn^{2+} concentration. Indirect trap-to-trap transfer, present in $RbMnF_3$, is not probable in the nonstoichiometric samples due to the increased presence of quenching sites.

I. INTRODUCTION

A significant property of stoichiometric Mn^{2+}-based materials is that the high concentration of the optically active Mn^{2+} ions does not result in a quenching of the luminescence emission. In many well-studied materials (e.g., Al_2O_3:Cr^{3+}, YAG:Nd^{3+}), strong luminescence quenching occurs as the concentration of optically active ions is increased. That is, the excitation is more and more easily transferred to sinks. This usually restricts the concentration of these ions, in laser crystals, for example, to less than 1 at. %.[1] The persistence of luminescence in Mn is a rarity among optically active constituents of ionic crystals.

Not only is this Mn emission of obvious interest based on its own merit, but its existence also provides a means of probing the rapid transfer of energy among optically active ions in stoichiometric crystals.

A stoichiometric Mn^{2+}-based crystal emits its dominant sharp-line luminescence from localized impurity-induced traps.[2] Since the traps are present in concentrations on the order of only ten parts per million, the excitation must be efficiently transferred to these localized sites. We have taken advantage of this feature in Mn^{2+} by directing our efforts toward a study of the transfer of excitation among Mn^{2+} ions as a function of their concentration; the systems investigated in this work are $RbMn_xMg_{1-x}F_3$: $x=1.0$, 0.8, and 0.4.

The stoichiometric crystal $RbMnF_3$ is antiferromagnetic with a Néel temperature of ~ 82 K. It possesses a cubic perovskite structure; the Mn^{2+} ion sits at the body center while the eight Rb^+ and six F^- ions, respectively, occupy the corners and face centers.

The emission of stoichiometric Mn-based crystals, including $RbMnF_3$,[3-9] has been the subject of much investigation over the past two decades. (For a review, see Ref. 10.) In contrast, however, similar studies applied to the case of nonstoichiometric crystals appear to be limited to the work of Koumvakalis *et al.*[11]

The results of the present study extend the current understanding of Mn-based crystals, especially in the area of nonstoichiometric crystals. It also presents a model for the deexcitation mechanism in $RbMn_xMg_{1-x}F_3$ from which quantitative estimates of the concentration dependence of the excitation transfer rate are derived.

II. EXPERIMENTAL TECHNIQUES

The absorption spectrum was obtained by means of a Cary Model 14R spectrometer. The luminescence spectra were obtained by exciting the sample, mounted in a Janis 8DT cryostat, with a GE Quartzline DVY 650W source, filtered through a $CuSO_4$ solution (3500—5300-Å bandpass). The luminescence was observed at 90° to the direction of excitation, filtered through a Schott-Ealing no. 26-4358 cutoff filter, chopped and focused onto the entrance slit of a Model 2051 McPherson scanning monochromator (blazed at 1.25 μm). (The resolution of the monochromator was ~ 4 Å.) The signal was detected by an RCA 7265 photomultiplier (S-20 response), amplified by a PAR Model 122 phase-sensitive detector and then displayed on a Cole-Parmer strip-chart recorder. With an instrumental time constant of 5 msec, the noise was minimal. The excitation measurements were performed by selectively pumping the sample under consideration with the Quartzline source in conjunction with a Model 82-410 Jarrell-Ash scanning monochromator (blazed at 0.6 μm) and then detecting the luminescence output by means of proper interference filters. For the excitation spectra, a dry-ice-cooled RCA 7102 photomultiplier tube (S-1 response) was employed.

The pulsed-luminescence measurements were made by exciting the sample with a Xenon Novatron 185C flashtube. The Mn emission was monitored by use of appropriate interference filters in conjunction with the RCA 7102 photomultiplier and then observed and photographed on a Tektronix Model 531 oscilloscope with a type-H plug-in. Measurements were also made using a Molectron Model UV12 nitrogen-pumped DL14 dye laser. The signal was detected by the RCA 7265 P/M via the McPherson monochromator which was set at the appropriate wavelength. The electrical signal was directed to a PAR Model 164

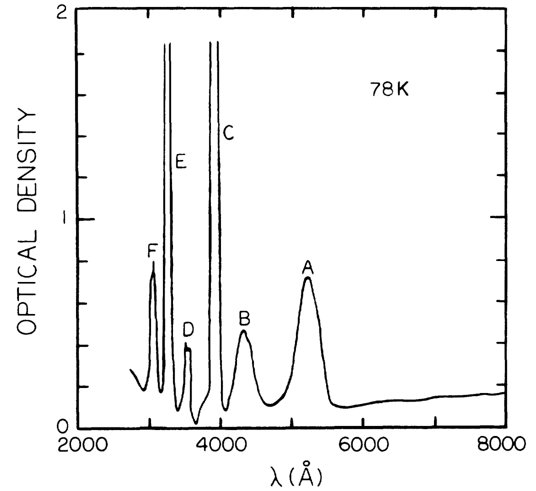

FIG. 1. Absorption spectrum of $RbMnF_3$ at 78 K.

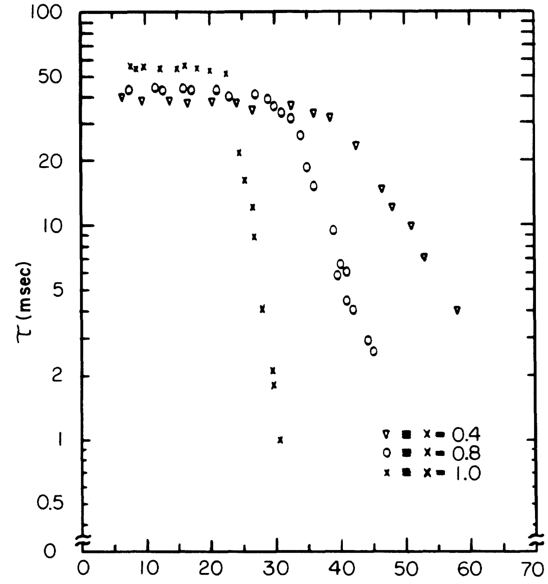

FIG. 3. Thermal dependence of the lifetime of the upper-energy emission band of $RbMn_xMg_{1-x}F_3$.

gated integrator connected to a PAR Model 162 boxcar averager. The temperature of the sample was varied from 4 to 120 K by means of an exchange-gas technique.

III. EXPERIMENTAL DATA

The optical-absorption spectrum of $RbMnF_3$ at 78 K appears in Fig. 1. The bands are labeled *A*—*F* according to the nomenclature developed by Mehra and Venkateswarlu[12] in their studies of the crystal.

The thermal dependence of the luminescence spectrum of the nominally pure Mn system $RbMnF_3$ is depicted in Fig. 2. The highly temperature-dependent emission of the crystal consists of (i) two broadbands (full width at half maximum $\sim 10^3$ cm^{-1}) that peak at approximately 5750 and 6440 Å and (ii) a number of sharp lines in the spectral range 5500—6000 Å.

With regard to the broad-emission bands of the crystal, the pulsed-luminescence measurements, shown in Figs. 3 and 4, reflect the fact that each may be associated with a single lifetime at any given temperature. The only exception is that a *luminescence rise* in the lower-energy band precedes an otherwise purely single-exponential decay in the temperature ranges ~7—10 and ~20—30 K. The lifetime data are in agreement with Gooen *et al.*[4] Excitation measurements indicate that both of these distinct bands are excited via the absorption bands of Mn.[4,9]

Referring back to Fig. 2, one will note that after a slight increase in the intensity from 9 to 11 K the higher-energy emission decreases rapidly with increasing temperature. This thermal quenching is accompanied by the *temperature enhancement* of the lower-energy emission band. Such an enhancement of the lower-energy emission, seen in other Mn-based crystals,[13] was first reported in $RbMnF_3$ by Danko *et al.*[9] In fact, at 28 K only the lower-energy band remains. At that point, this intensity of the band is comparable to that once achieved by the higher-energy band at low temperature. This thermal

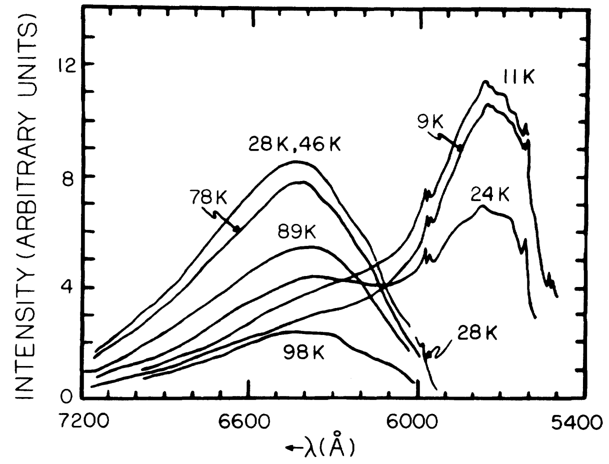

FIG. 2. Thermal dependence of the luminescence spectrum of $RbMnF_3$.

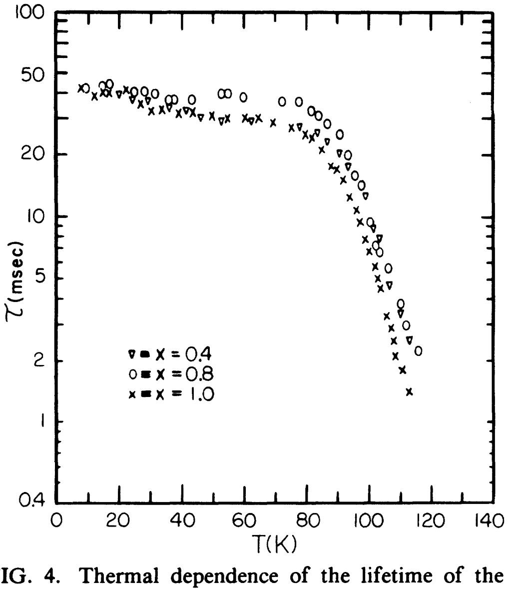

FIG. 4. Thermal dependence of the lifetime of the lower-energy emission band of $RbMn_xMg_{1-x}F_3$.

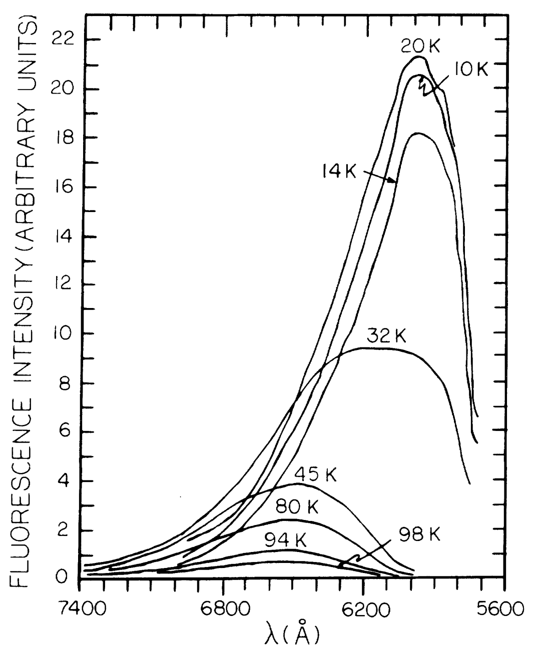

FIG. 5. Thermal dependence of the luminescence spectrum of $RbMn_{0.8}Mg_{0.2}F_3$.

enhancement of the lower-energy band takes place in the same temperature range in which the band, in response to pulsed excitation, exhibits a luminescence rise. The corresponding effect on the higher-energy emission band is reflected in a *thermal falloff* of its own lifetime.

The lower-energy band of $RbMnF_3$ eventually decreases with further increase in temperature, in accord with its lifetime dependence on temperature, becoming relatively weak around 120 K. With regard to the sharp-line luminescence structure of $RbMnF_3$, it is noted that the structure appears to be thermally quenched by ~30 K.

The introduction of a Mg concentration of 20 at. % results in a thermal dependence of the luminescence spectrum as shown in Fig. 5. Once again, using lifetime measurements (refer to Figs. 3 and 4), one is able to detect the presence of *two* distinct temperature-dependent emission bands; the more energetic band thermally quenches at low temperature, followed by the quenching of the remaining band by ~120 K. As with $RbMnF_3$, excitation measurements indicate that both bands are activated via the absorption bands of Mn. This lower-energy band, seen as a "shoulder" to the higher-energy emission by Koumvakalis *et al.* in their studies of $RbMn_{0.7}Mg_{0.3}F_3$ and $RbMn_{0.4}Mg_{0.6}F_3$,[11] is, in fact, a second distinct emission band.

In contrast to the fully concentrated system $RbMnF_3$, the following features of $RbMn_{0.8}Mg_{0.2}F_3$ are noted.

(i) No sharp-line structure is present.

(ii) The peak positions of the two emission bands are shifted toward longer wavelengths (5750→6000 Å and 6440→6500 Å).

(iii) A luminescence rise is no longer detectable. Both bands now exhibit a single decay throughout the temperature range studied.

(iv) The higher-energy emission has a slower falloff with increasing temperature and is thermally quenched at a higher temperature (45 vs 28 K). This is reflected in Fig. 3.

(v) The low-temperature lifetime of the higher-energy band is reduced from 55 to 43 msec.

(vi) The thermal dependence of the lifetime of the lower-energy emission band is noticeably unaffected.

(vii) Enhancement of the lower-energy band does not accompany the quenching of the higher-energy emission nor does the peak intensity of this lower-energy band ever reach more than a fraction of that once achieved by the higher-energy emission at low temperature.

As portrayed in the spectra of Fig. 6 and the lifetime data of Figs. 3 and 4, a further increase in the Mg^{2+} concentration from 20 to 60 at. % results in few new features. Two distinct, featureless emission bands, activated via the absorption bands of Mn, are present with no further shift in position. Quenching of the higher-energy band occurs at low temperature followed by the quenching of the lower-energy band at the usual 120 K. A slight increase in intensity occurs in the higher-energy band, prior to its thermal quenching, in the range 5—28 K.

In agreement with the spectral trends exhibited by the previous step down in Mn concentration, the following are true.

(i) No sharp-line structure is present.

(ii) No luminescence rise is detected. Both bands exhibit a single decay throughout the temperature range studied.

(iii) The higher-energy emission has an even slower falloff with increasing temperature and is thermally quenched at a higher temperature (~60 K).

(iv) The low-temperature lifetime of the higher-energy band is further reduced (to 38 msec).

(v) The thermal dependence of the lifetime of the lower-energy emission band remains relatively unaffected.

(vi) Enhancement of the lower-energy band does not accompany the quenching of the higher-energy emission, nor

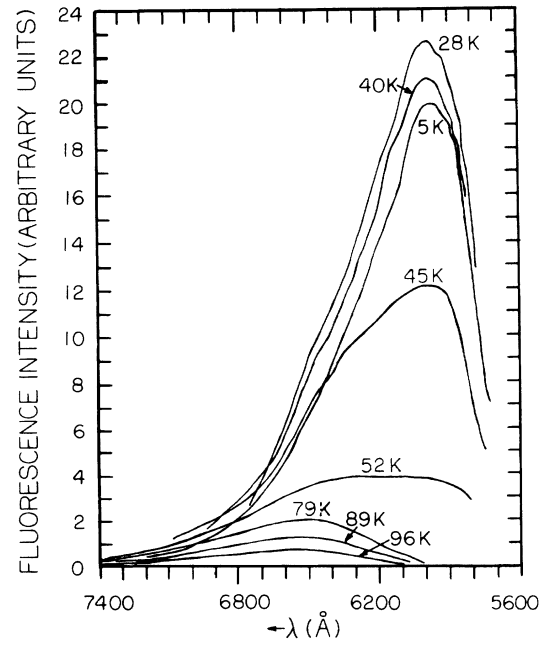

FIG. 6. Thermal dependence of the luminescence spectrum of $RbMn_{0.4}Mg_{0.6}F_3$.

does the peak intensity of this lower-energy band ever reach more than a fraction of that once achieved by the higher-energy emission at low temperature.

The position and thermal dependence of the higher-energy luminescence band of $RbMn_{0.4}Mg_{0.6}F_3$ is in agreement with Koumvakalis *et al.*[11] However, with regard to the lifetime of the band, we report a slightly longer low-temperature value (38 vs 33 msec) and a slightly steeper falloff with increasing temperature. For temperatures above ~50 K, the data are in agreement.

IV. INTERPRETATION OF RESULTS

A. Discussion of general spectral features

The sharp-line emission structure of $RbMnF_3$, shown in Fig. 2, represents electronic and magnon-assisted transitions at impurity-induced localized Mn^{2+} luminescence centers (i.e., traps).[9] For this reason, the emission is referred to as *extrinsic* Mn luminescence. (The much weaker *intrinsic* luminescence lines, i.e., exciton and magnon-assisted exciton lines, have been detected in the spectral range ~5480–5550 Å.[5–8])

The lack of sharp-line emission in the two nonstoichiometric Mn crystals is not surprising. First of all, due to the significant increase in the average spacing between Mn ions in the latter crystals over that in $RbMnF_3$, it is expected that the probability of a magnon-assisted transition is substantially reduced. This would be reflected in a substantial reduction of the intensity of all magnon sidebands, including the extrinsic 1-magnon sidebands which dominate the observed sharp-line structure in $RbMnF_3$.[9] Secondly, the increased Mg concentration is expected to result in an inhomogeneous broadening of the sharp emission lines. In fact, based on the work of Hegarty *et al.* on MnF_2:Zn,[14,15] the strain due to such a high concentration of Mg^{2+} ions in the two nonstoichiometric crystals should be sufficient to broaden all remaining sharp lines beyond the level of detection. Since the sharp lines do not survive the increase in Mg concentration, then obviously the present study is limited in scope to an investigation of the broadbands.

The bulk of the luminescence of $RbMnF_3$ may be attributed to Mn emission from two distinct, localized traps. The broad-emission bands represent multiphonon sidebands of the transitions from the trap levels to the ground state. It seems reasonable to assume the same nature for these bands in the nonstoichiometric crystals. The effect of a decreasing Mn^{2+} concentration on the peak position of the two broad-emission bands is probably due in part to their complex composition.

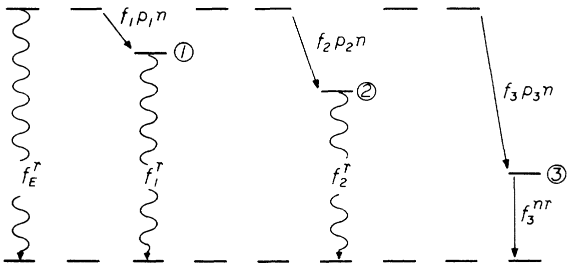

FIG. 7. Deexcitation model.

The remaining characteristics of $RbMn_xMg_{1-x}F_3$ are the following: (i) a higher quenching temperature for the higher-energy emission band with decreasing Mn^{2+} concentration, (ii) a relative insensitivity of the lifetime of the lower-energy emission to the Mn^{2+} concentration, and (iii) the lack of a temperature enhancement of the intensity of the lower-energy band and the lack of a luminescence rise in the response of this band to pulsed excitation in the nonstoichiometric crystals.

B. Rate-equation analysis

The fact that localized Mn traps, present in $RbMnF_3$ at a concentration on the order of only ten parts per million, are responsible for nearly all of the luminescence of the crystal is direct evidence of the existence of an efficient transfer of excitation among the relatively unperturbed Mn^{2+} ions in the stoichiometric crystal. This transfer rate should decrease with decreased Mn concentration.

Since the broad-emission bands represent phonon-assisted transitions from two such traps, then a study of the lifetime behavior of these bands in $RbMn_xMg_{1-x}F_3$ may lend itself to a determination of the Mn^{2+} concentration dependence of the rate of excitation transfer to the luminescing traps.

In order to gain some insight into the energy transfer in $RbMn_xMg_{1-x}F_3$, it is assumed that the energy-level scheme of Fig. 7 is representative of the situation at hand. Three types of localized traps, labeled $i=1$, 2, and 3, are present. Above the trap levels is the first excited energy level of the unperturbed Mn^{2+} ions. Trap i has a depth ΔE_i, a probability of existence p_i, and an excited-state population N_i. Radiative- and nonradiative-transition rates from a given excited level to the ground level of a trap are denoted as f_i^r and f_i^{nr}, respectively. The unperturbed Mn^{2+} ions possess a total excited-state population N_E. The radiative-transition rate from such an excited level to the ground level of an ion is denoted as f_E^r. The rate of nonradiative transfer of excitation, at low temperature, from a (nearest-neighbor) unperturbed Mn^{2+} ion to a trap of type i is denoted as f_i. The symbol n refers to the

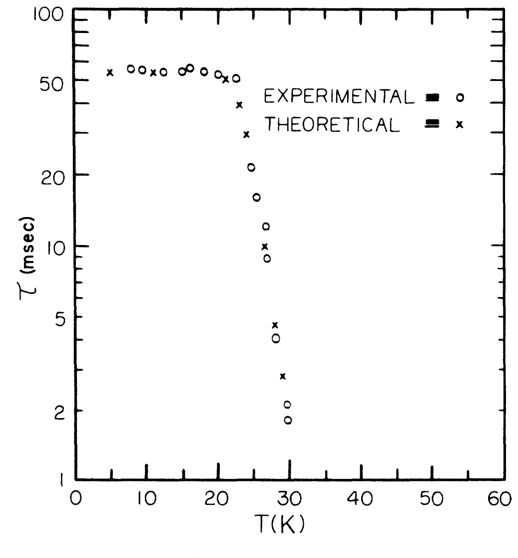

FIG. 8. Theoretical fitting of the temperature-dependent lifetime of the upper-energy emission band of $RbMnF_3$.

number of first-nearest-neighbor Mn ions. The traps are such that only the two shallowest ones emit in the visible; the third type of trap represents a quenching site.

In this model, the $RbMnF_3$ exciton line $E1$ represents the emission from the unperturbed Mn^{2+} ions. Apart from a Stokes shift, one would expect the purely electronic emission line from trap i to be spectrally located a distance ΔE_i below $E1$.

Provided the transfer of excitation from one ion to the next is not limited by diffusion, one may apply rate equations to such an energy-level scheme. At first let us consider those temperatures where thermal activation is possible only from the shallowest trap.

If absorption is terminated at time $t=0$, the rate equation for $t>0$ may be expressed as follows:

$$\frac{dN_E}{dt}=-N_E\left[f_E^r+\sum_{i=1}^{3}f_ip_in\right]+f_1(n-1)N_1\exp\left[-\frac{\Delta E_1}{KT}\right], \quad (1)$$

$$\frac{dN_1}{dt}=-N_1\left[f_1^r+f_1(n-1)\exp\left[-\frac{\Delta E_1}{KT}\right]\right]+f_1p_1nN_E, \quad (2)$$

$$\frac{dN_2}{dt}=-N_2f_2^r+f_2p_2nN_E . \quad (3)$$

One will note that direct trap-to-trap transfer is ignored due to the fact that the traps are present in relatively low concentrations. A radiationless decay to the ground state from the two shallower traps is assumed to be negligible.

Analytical solutions to the rate equations (1)—(3) are not difficult to obtain. A detailed solution, however, is not needed to explain our experimental results. We note simply that, if the unperturbed level $E1$ has a lifetime that is short compared with those of the trap levels 1 and 2, then the luminescence from these traps will decay asymptotically with lifetimes given by

$$\tau_1^{-1}=f_1^r+(n-1)f_1\exp\left[\frac{-\Delta E_1}{KT}\right], \quad (4)$$

$$\tau_2^{-1}=f_2^r . \quad (5)$$

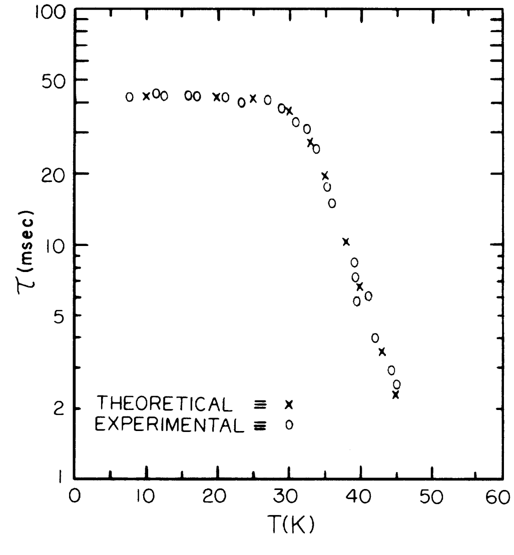

FIG. 9. Theoretical fitting of the temperature-dependent lifetime of the upper-energy emission band of $RbMn_{0.8}Mg_{0.2}F_3$.

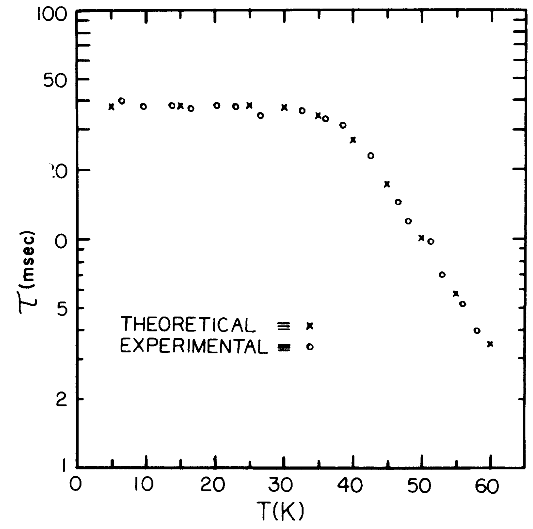

FIG. 10. Theoretical fitting of the temperature-dependent lifetime of the upper-energy emission band of $RbMn_{0.4}Mg_{0.6}F_3$.

The assumption of a relatively short lifetime for $E1$ is valid for the stoichiometric crystal $RbMnF_3$. Strauss *et al.*[7] report a value of 36 μsec for this level; the lifetimes of the emitting trap levels (Figs. 3 and 4) are much longer than this. The same must also be true for the nonstoichiometric crystals, since no emission is observed from the unperturbed Mn^{2+} ions.

For temperatures *above* that corresponding to the quenching of the higher-energy band of each crystal, only one luminescence trap "effectively" remains. One *might* expect the lifetime of the lower-energy band of $RbMn_xMg_{1-x}F_3$ to exhibit a behavior similar to (4). That is,

$$\tau_2^{-1}=f_2^r+(n-1)f_2\exp\left[\frac{-\Delta E_2}{KT}\right] . \quad (6)$$

(Note that, as before, a radiationless decay at site 2 is assumed to be negligible.)

C. Detailed interpretation of emission spectral characteristics

The lifetime of the higher-energy luminescence band of $RbMn_xMg_{1-x}F_3$ was found to indeed exhibit a thermal

TABLE I. Fitting parameters for the lifetime of the $RbMn_xMg_{1-x}F_3$ higher-energy emission band.

at. % Mn^{2+}	ΔE (cm^{-1})	f_1^r (sec^{-1})	$(n-1)f_1$ (sec^{-1})
100	300±5	18.2±0.3	$(1.0\pm0.25)\times10^9$
80	294±7	23.3±0.5	$(5.0\pm1.0)\times10^6$
40	265±6	26.3±0.8	$(1.5\pm0.2)\times10^5$

TABLE II. Fitting parameters for the lifetime of the $RbMn_xMg_{1-x}F_3$ lower-energy emission band above T_q. (T_q denotes the quenching temperature of the higher-energy emission.)

at. % Mn^{2+}	ΔE (cm^{-1})	f_2^r (sec^{-1})	$(n-1)f_2$ (sec^{-1})
100	830±20	31.3±0.5	$(2.2\pm0.6)\times10^7$
80	830±20	25.0±2.5	$(1.2\pm0.3)\times10^7$
40	830±20	34.0±0.7	$(1.1\pm0.3)\times10^7$

dependence as described by Eq. (4) and indicates that the higher-energy emission quenches by thermal activation to the $E1$ level. These fittings are shown in Figs. 8—10, while the values of the fitting parameters appear in Table I. We note the following trends: (1) the increase of f_1^r with increasing Mg^{2+} concentration and (2) the decrease in ΔE and f_1 with increasing Mg^{2+} concentration. The increase in f_1^r may reflect a perturbation of the trap-site environment which in turn enhances the downward radiative-transition probability. The decrease in ΔE may be indicative of a Mg strain-induced depression of the $E1$ level which is more severe than any additional effect on the trap level. Lastly and most importantly, the four-order-of-magnitude reduction in the trap transfer rate f_1, clearly portrays the diminishing strength of the Mn-trap coupling. [Table I presents values for the product $(n-1)f_1$. However, the exact value of n is not critical in our discussion. It does not reduce by an order of magnitude as the concentration of Mn^{2+} is reduced from 100 to 40 at. %, nor does it represent a large quantity, e.g., $n=6$ in $RbMnF_3$.]

It is also noted that up through the quenching temperature of the higher-energy emission band of the particular crystal in question, the lifetime of the $RbMn_xMg_{1-x}F_3$ lower-energy band is found, as predicted by Eq. (5), to be relatively temperature independent.

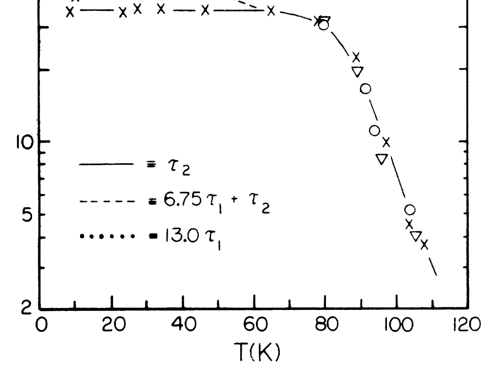

FIG. 11. Thermal dependence of the total integrated luminescence intensity of $RbMn_xMg_{1-x}F_3$ (corrected for instrumental spectral sensitivities).

The fitting of the lifetime data of the lower-energy emission band of $RbMn_xMg_{1-x}F_3$, at temperatures above that corresponding to the quenching of each higher-energy band of the crystal to the relation (6), was only fair. The values of the fitting parameters appear in Table II. In addition to only a fair fitting of the data, such a quenching model for the $RbMn_xMg_{1-x}F_3$ lower-energy emission band is deficient in two important respects. They are as follows.

(i) In contrast to an approximate four-order-of-magnitude decrease in the transfer rate to the shallow trap, the "transfer rate" to this deeper luminescence trap remains practically constant as the Mn^{2+} concentration is reduced from 100 to 40 at. %. This is physically unreasonable since the transfer rate is a function of the Mn-Mn coupling which decreases with increasing separation.

(ii) The "trap depth" is independent of the Mg^{2+} concentration and, as such, is not in agreement with the behavior mentioned earlier.

The quenching of the lower-energy emission band of $RbMn_xMg_{1-x}F_3$ is thus not by thermal activation to the $E1$ level, but is probably by a multiphonon decay to the ground level. The Mn^{2+} concentration would thus affect only the feeding of this deeper trap, not the quenching of its emission.

V. CONCLUDING REMARKS: RESONANT ENERGY TRANSFER

It can be concluded that an efficient non-diffusion-limited transfer of excitation exists in $RbMn_xMg_{1-x}F_3$ down to a concentration of at least 40 at. % Mn. This is evidenced by the applicability of a rate-equation approach and by the fact that these relatively sparse Mn traps continue to emit the bulk of the luminescence of each crystal.

The reduced indirect transfer of excitation between the two Mn luminescence traps in the nonstoichiometric samples (via the less-perturbed Mn^{2+} ions) is best indicated by reference to Fig. 11. This figure depicts the total integrated luminescence intensity (in number of photons emitted) for each of the three crystals at temperatures up to 110 K. (The total integrated luminescence intensity is equal to the area under the luminescence intensity versus the λ curve, the curve first being corrected for instrumental spectral sensitivities and by the factor λ.) Normalization of the integrated intensity data of each sample was such as to clearly depict the existence of the same thermal dependence beyond, e.g., 70 K, as that of τ_2. This dependence is not surprising since it is only the lower-energy band that emits in these crystals in this temperature range. The result of this normalization is that the total integrated luminescence intensity of $RbMnF_3$ exhibits a thermal behavior like τ_2, $RbMn_{0.8}Mg_{0.2}F_3$ like $(6.75\tau_1+\tau_2)$, and $RbMn_{0.4}Mg_{0.6}F_3$ like $13\tau_1$ for $T<65$ K.

It is apparent from Fig. 11 that the integrated intensity of the 100-at. % Mn sample remains relatively constant well beyond the quenching temperature of its higher-energy luminescence band. This indicates that the deeper luminescence trap gains all the energy that is thermally activated from the shallower luminescence trap. Trap-to-trap nonradiative transfer, via the less-perturbed Mn ions, is thus totally efficient. Since thermal quenching of the lower-energy band is by a downward multiphonon decay, then it would appear that the quenching traps of $RbMnF_3$ play an insignificant role in robbing the crystal of potential luminescence output.

The lack of constancy in the total integrated intensity of the nonstoichiometric crystals, once the higher-energy band starts to quench, is indicative of the fact that the energy which is thermally activated from the shallower luminescence trap simply does not make it to the deeper luminescence trap. Therefore, the total integrated intensity falls off with increasing temperature much like that of the higher-energy band. Although the transfer among Mn ions, down to a Mn concentration of 40 at. %, is efficient, as previously concluded, it must be that an increased number of quenching sites are introduced during the growth process of the nonstoichiometric crystals which rob the crystal of potential luminescence output in this temperature range.

ACKNOWLEDGMENTS

This research was supported in part by North Atlantic Treaty Organization Research Grant No. 1169. The authors would like to thank Dr. J. Martin and Dr. W. Sibley for providing some of the crystals studied in this investigation.

---

[1] L. Riseberg, in *Radiationless Processes,* edited by B. DiBartolo (Plenum, New York, 1980), pp. 369—407.

[2] R. Greene, D. Sell, R. Feigelson, G. Imbusch, and H. Guggenheim, Phys. Rev. 171, 600 (1968).

[3] W. Holloway, E. Prohofsky, and M. Kestigian, Phys. Rev. 139, A954 (1965).

[4] K. Gooen, B. DiBartolo, M. Alam, R. Powell, and A. Linz, Phys. Rev. 177, 615 (1969).

[5] M. Chen, D. McClure, and E. Solomon (unpublished report), as referenced in Phys. Rev. B 4, 3141 (1971).

[6] S. Stokowski, D. Sell, and H. Guggenheim, Phys. Rev. B 4, 3141 (1971).

[7] E. Strauss, V. Gerhardt, and H. Riederer, J. Lumin. 12/13, 239 (1976).

[8] T. Chiang, P. Salvi, J. Davies, and Y. Shen, Solid State Commun. 26, 527 (1978).

[9] J. Danko, D. Pacheco, and B. DiBartolo, J. Lumin. (in press).

[10] R. Moncorgé and B. Jacquier, in *Collective Excitations in Solids,* edited by B. DiBartolo and J. Danko (in press).

[11] N. Koumvakalis, W. Sibley, and G. Venikouas, J. Lumin. 15, 283 (1977).

[12] A. Mehra and P. Venkateswarlu, J. Chem. Phys. 47, 2334 (1967).

[13] V. Goldberg, R. Moncorgé, D. Pacheco, and B. DiBartolo, in *Luminescence of Inorganic Solids,* edited by B. DiBartolo (Plenum, New York, 1977).

[14] J. Hegarty, Ph.D. thesis, University College at Galway, 1976 (unpublished).

[15] J. Hegarty, B. A. Wilson, W. M. Yen, T. J. Glynn, and G. F. Imbusch, Phys. Rev. B 18, 5812 (1978).