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Perturbed Mn^{2+} transitions in irradiated $RbMgF_3$:Mn†

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A study of the optical transitions of radiation-induced *F*-center–Mn^{2+} pairs in $RbMgF_3$:Mn crystals has been made. The temperature dependence of the absorption, the emission and excitation spectra of this defect complex was investigated, and the oscillator-strength enhancement of Mn^{2+} caused by the next-neighbor radiation-induced defect determined. This oscillator-strength change, which is due to exchange interaction, is about 10^4. The thermal annealing of the radiation defects is also reported.

INTRODUCTION

The apparently large oscillator strength changes which occur in 3*d* impurity ions when radiation defects are present can be important in numerous device applications if an understanding of the effect can be achieved. Recently,[1] we have shown that in $KMgF_3$ all Mn^{2+} and some Co^{2+} transitions are enhanced by exchange interactions between *F* centers and the 3*d* impurities, and the work of Young *et al.*[2] indicates that in irradiated $KMgF_3$:Mn one set of perturbed Mn^{2+} transitions is due to *F*-center–Mn^{2+} pairs.[1,3] In fact, these perturbed optical transitions are very similar to the unperturbed Mn^{2+} transitions studied by McClure, Ferguson, and others.[4-7]

In a previous investigation[8] of irradiated $RbMgF_3$ it was determined that, even though *F* centers are produced by photochemical means, these centers, in contrast to those in $KMgF_3$ and MgF_2,[9,10] are not mobile at room temperature. Empty negative-ion vacancies are not mobile at this temperature either. In that work[8] it was possible to identify the optical absorption due to *F* centers F_2, F_3, and $[X_2^-](V_k)$ centers. Thermal-annealing studies showed that *F* centers aggregated in this material to form F_2 centers at about 425 K if the sample was kept in the dark. Aggregation occurred at lower temperature if *F* light (300 nm) was used to illuminate the sample during heat treatment. Because of the lack of *F* mobility it was felt that this host crystal would be ideal for determining the relative oscillator strengths of the perturbed Mn^{2+} transitions and the *F* center, as well as the mechanism of *F*-center aggregation. Thus, the purpose of this paper is to report experiments on the formation and character of perturbed Mn^{2+} bands in $RbMgF_3$ and to give additional information on the kinetics of defect formation in this type of crystal.

EXPERIMENTAL PROCEDURE

In order to perform this investigation it was necessary to have available single crystals of $RbMgF_3$ doped with various concentrations of manganese impurity. These crystals were grown by J. J. Martin in the Oklahoma State University Crystal Growth Laboratory using conditions previously described.[8] Most of the information in this paper is derived from crystals containing about 0.2-at.% manganese. After growth the crystals, which have hexagonal structure, were analyzed with a polarizing microscope to determine the optic axis and were cut and polished with the optic axis perpendicular, $C_\perp$, or parallel, $C_\parallel$, to the crystal face. The samples were irradiated with 1.5-MeV electrons at a current of about 0.2 $\mu A/cm^2$. For both irradiation and measurement the crystals were placed in a cryogenerator or a standard helium cryostat. The temperature of the cryogenerator could be controlled to ±1 K between 15 and 300 K. The cryogenerator lacked the necessary cooling power to maintain the sample at 15 K during irradiation. However, measurements made during irradiation indicated the sample temperature was never higher than 35 K. Optical absorption was measured using a Cary 14 spectrophotometer and emission was detected with a 1-m Jarrell-Ash monochromator and associated electronics. Excitation spectra were taken by exciting the sample with light from a Spex 22-cm monochromator. Polarization data were obtained using unsupported HNP'B Polaroid ultraviolet sheets.[1,8] The exciting source, a 75-W xenon lamp, was calibrated for intensity versus wavelength and the excitation spectra have been corrected for this effect. Optical bleaching of irradiated crystals was accomplished with light from a 100-W mercury lamp passed through 300- or 433-nm interference filters. Thermal-annealing experiments consisted of holding the specimens at a certain temperature for 10 min and then cooling in air to room temperature.

RESULTS

When nominally pure or doped $RbMgF_3$ crystals are irradiated with electrons at 300 K only the optical-absorption band at 295 nm (4.2 eV) with width at half-maximum, W, of 0.95 eV is observed to increase with radiation dose. Figure 1 illustrates the growth of this band as a function of temperature for both pure and Mn-doped crystals. The number of *observable* F centers at a given radiation dose is obviously less in the Mn-doped material; however, other "pure" samples have growth curves similar to that shown for the Mn-doped material. When irradiated samples are annealed a definite difference in behavior is noted between doped and pure material (Fig. 2). Figure 2(a) depicts the effects of annealing on the F centers and the aggregation of F_2 and F_3 centers in nominally pure samples, whereas, Fig. 2(b) portrays the annealing of F centers and the formation of the defect complex responsible for a series of absorption bands at 600, 425, 343, 328, 297, and 273 nm in doped specimens. In the figure the growth of the 425-nm band is plotted although the others also grow in simultaneously. F_2 and F_3 bands are also observed to appear in the impurity-doped samples at about the same temperature as for the undoped material, but these bands are much smaller due to the competition from the presence of Mn^{2+}. The series of absorption bands present in the heat-treated doped crystals is shown in Fig. 3 and can be eliminated by optical bleaching with light of wavelength shorter than 350 nm. At 77 and 300 K a 433-nm optical bleach does not decrease the intensity of this series of bands, but 2 h bleaching with 300-nm light causes it to disappear completely leaving only the small F_3 band visible at 300 nm. It was also found that it was possible to bleach out the small F_2 band with 433-nm light at 300 K. Heat treatment to about 500 K returns the series of bands to 60% of its original intensity, but treatment at higher temperatures evidently destroys the complex. In Fig. 2 it should be noted that the F band is reduced more rapidly for the impure specimens than for the pure ones. In an effort to determine whether this annealing is due to interstitial-vacancy recombination or to valence changes a sample was irradiated at 300 K and then heat treated for 10 min at 500 K with a resultant loss of F centers. The sample was then given a very short (60 sec) reirradiation with 1.5-MeV electrons and no recovery of the F band was observed. This suggests that some type of interstitial-vacancy motion occurs and the ap-

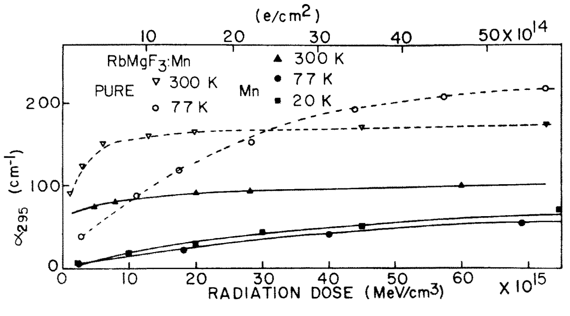

FIG. 1. F-center absorption, α_{295}, as a function of absorbed energy for pure (open symbols) and Mn-doped (solid symbols) crystals electron irradiated at 77 and 300 K.

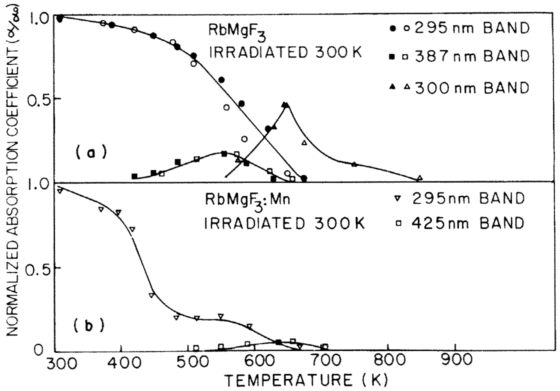

FIG. 2. (a) Normalized thermal-annealing data for nominally pure $RbMgF_3$ samples eletron irradiated to different doses. (b) Normalized thermal-annealing data for $RbMgF_3$: Mn specimens.

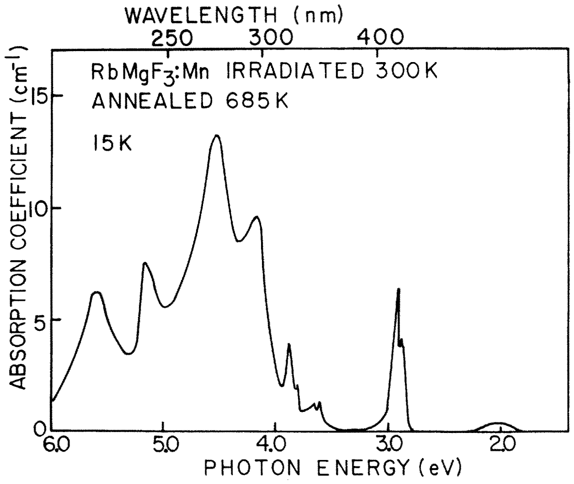

FIG. 3. Optical absorption at 15 K for $RbMgF_3$: Mn sample electron irradiated at 300 K and annealed 10 min at 685 K. In order to show all the bands a specimen cut with the c axis 45° to the crystal face was used.

parent loss of F centers is not due to simple valence changes.

After a doped sample is heated to about 650 K as indicated in Fig. 2(b) the series of lines mentioned above appears. Concurrently, optical-emission bands are observed at 720 nm (1.72 eV) and 840 nm (1.47 eV) as can be seen in Fig. 4. An emission band at 560 nm (2.2 eV) is also present but it is difficult to state, because of the low intensity, whether this band increases with heat treatment or not. The 720-nm band is the most easily observed and is similar to an emission band that appears in manganese-doped MgF_2 and $KMgF_3$.[1,3] The excitation spectrum of this emission band is shown in Fig. 5. The temperature dependence of the intensities of the excitation bands and the emission bands is shown in the insets of Fig. 4 and 5. The excitation spectrum for the 840-nm band is illustrated in Fig. 6.

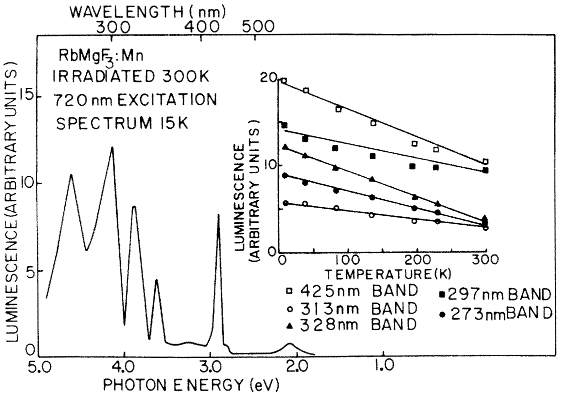

FIG. 5. Excitation spectrum at 15 K for the 720-nm emission band in the crystal used for the data in Fig. 4. The inset shows the temperature dependence of the bands.

DISCUSSION

An inspection of Fig. 1 reveals that the apparent F-center production at 77 K in Mn-doped crystals is suppressed compared to that in pure specimens. There is also some difference in the 300-K growth curves, but since the variation of the growth curves for the various "pure" boules is so great it is not clear that this is meaningful. It is not obvious, however, whether this apparent decrease is the result of a suppression of the production mechanism, enhanced interstitial-vacancy recombination, or valence changes which leave some negative-ion vacancies without electrons. The annealing curve in Fig. 2(b) for F centers in impure crystals does show a recombination anealing stage at a temperature below that at which F centers are generally mobile [see Fig. 2(a)]. Since this lower-temperature recovery stage does result in the destruction of the F centers perhaps it is due to the release of impurity-trapped interstitials or to F centers moving to nearby trapped interstitials.

If we assume that in the case of nominally pure crystals the interstitials produced during irradiation cluster into large aggregates and the vacancies because they are immobile at room temperature have a statistical distribution in the lattice then it is possible to calculate the relative oscillator strengths of F, F_2 , and F_3 centers. For example, let us first consider the F and F_2 centers. One of the F_2-center transitions occurs at 387 nm and has a half-width of $W_{F_2} = 0.29$ eV while the F center absorbs at 295 nm and has $W_F = 0.95$ eV. Thus, for the temperature range of 425–565 K in Fig. 2(a) if we assume all the F centers which are

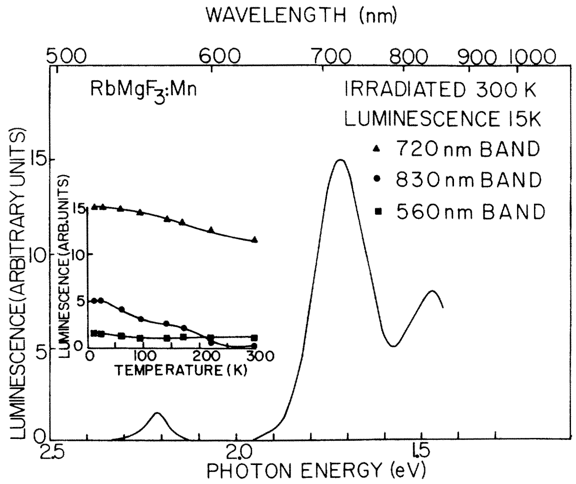

FIG. 4. Emission spectrum at 15 K from a crystal irradiated at 300 K annealed to 685 K, and excited with 425-nm light. The inset illustrates the temperature dependence of the intensity of the three bands.

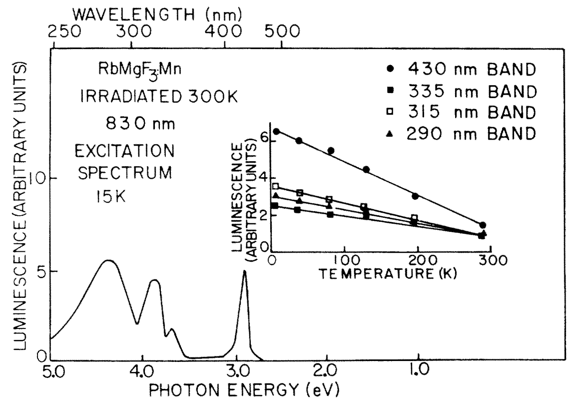

FIG. 6. Excitation spectrum at 15 K for the 840-nm emission in the crystal used for the data in Fig. 4. The inset shows the temperature dependence of the excitation peaks.

TABLE I. Observed and calculated energies for Mn^{2+} terms for $RbMnF_3$ (Ref. 7) and $RbMgF_3:Mn$.

Level	Calculated energy (with spin-orbit) (cm^{-1})	Observed energy 77 K (cm^{-1})	f	Irradiated $RbMgF_3:Mn$ (1 at. %) 15 K (cm^{-1})	f	Predicted polarization
$^4A_2(^4F)$	40 117	41 158		36 693		z
$^4T_1(^4P)$	32 887	39 700				
	32 848	38 000				
	32 781	32 798	1.5×10^{-7}	33 629		x, y
	32 780	32 446				
$^4E(^4D)$	29 657	30 478				
	29 588		1.5×10^{-7}	31 209	$\sim10^{-3}f_F$[b]	z
	29 561	30 140				
$^4T_2(^4D)$	27 891	28 385		30 645		
	27 802	28 258	1.1×10^{-7}	29 435		x, y
	27 601	28 129		29 113		
	27 590	27 917				
$^4A(^4G)$	23 977[a]	25 759				
		25 543	9.2×10^{-7}	23 669	$0.05f_F$[b]	z
$^4E(^4G)$	23 990	25 336		23 580	$0.05f_F$[b]	
	23 989		9.2×10^{-7}			
	23 982	23 195		23 250	$0.05f_F$[b]	z
$^4T_2(^4G)$	21 968					
	21 965	23 106	1.6×10^{-7}			
	21 880					
	21 840					
$^4T_1(^4G)$	18 236					
	18 197	19 150	2.0×10^{-7}	16 451	$\sim10^{-3}f_F$[b]	x, y
	18 142					
	18 126					
$^6A(^6S)$						

[a] In $KMgF_3:Mn$ Ferguson *et al.* (Ref. 6) observe the ^4E transition lowest.

[b] f_F, the F-center oscillator strength, is most likely between 0.5 and 1.

lost form F_2 centers at a rate of $2\Delta N_{F_2}=\Delta N_F$, then from Smakula's equation[11] $N_i f_i = 0.87\times10^{17} C_i W_i \alpha_i$, where C_i is the same for each band, we find

$$\frac{(\Delta N_F)f_F}{(\Delta N_{F_2})f_{F_2}}=\frac{W_F(\Delta\alpha_F)}{W_{F_2}(\Delta\alpha_{F_2})},$$

$$f_{F_2}(387)=0.28f_F.$$

For the F_3 transition at 300 nm with $W_{F_3}=0.33$ eV and $\Delta N_F=\Delta N_{F_3}$,

$$\frac{\Delta N_F f_F}{\Delta N_{F_3} f_{F_3}}=\frac{W_F\Delta\alpha_F}{W_{F_3}\Delta\alpha_{F_3}},$$

$$f_{F_3}=0.31f_F.$$

If the case of $\Delta N_{F_2}=\Delta N_{F_3}$ is considered, fair agreement is obtained with the previous case of $\Delta N_F=\Delta N_{F_3}$. This agreement in f values whether we consider F or F_2 centers in calculating f_{F_3} is pleasing. Obviously, the calculation is only valid if no F centers are lost to sources other than vacancy aggregation. As a check to determine if vacancies are conserved during the annealing process we gave a brief reirradiation to a crystal which was heat treated to 650 K and found that the cluster centers were destroyed and the F-center concentration was reproduced to within 5% of the original concentration prior to heat treatment. This suggests that the approximation is valid. When samples are heated above 700 K there is a definite loss of F centers suggesting vacancy-interstitial recombination at the higher temperatures. A review of F_2-center oscillator strengths is given by Compton and Rabin.[11] The oscillator strength of the F_2 center in KCl as measured by Ohkura,[12] Tomiki,[13] Delbecq[14] is 0.23 with the oscillator strength of the F center taken as 0.53. For the same f_F value our calculation gives $f_{F_2}(387)=0.15$.

Since vacancies are not mobile at 300 K in $RbMgF_3$ the probability of observing F-center-Mn^{2+} complexes after irradiation at this temperature depends on the following statistical relationship:

$$N_{F\text{-Mn}} = 6N_{\text{Mn}}N_F/N_0,$$

where N_i denotes the concentration of the ith-type defect and N_0 is the concentration of negative-ion sites in the crystal. Since our samples contain at most 1 at.% Mn^{2+} we find $N_{F\text{-Mn}} = 2\times10^{-2}N_F$. If the oscillator strength of the F center is assumed to be unity, then from Fig. 1 N_F is determined to be $N_F \simeq 10^{18}$ cm^{-3} and $N_{F\text{-Mn}} \simeq 10^{16}$ cm^{-3}, which would be difficult to observe in absorption even for an oscillator strength of unity. However, when the vacancies become mobile at higher temperatures aggregation can occur and the $N_{F\text{-Mn}}$ concentration should increase.

The series of bands which appears upon heat treatment of Mn-doped crystals is remarkably similar in both absorption and emission to that in $KMgF_3$:Mn.[1] Table I gives the observed Mn^{2+} transitions in $RbMnF_3$ and their oscillator strengths. Also shown are the transition-energy values for our data of Fig. 3. Figure 7 illustrates the polarization dependence of the various transitions as measured from a $C_{\parallel}$ crystal with the 90° reading corresponding to the case with the electric vector E perpendicular to the optic or C axis. Note that the nature or order of these polarizations agrees with what is predicted for Mn transitions. The fact that optical bleaching destroys these transitions is also in accord with what has been observed previously in $KMgF_3$:Mn.[1] This suggests that the transitions are due to perturbed Mn^{2+} centers and that the oscillator-strength enhancement is due to exchange.[1] It is most interesting to note that as the F centers migrate to the Mn^{2+} ions the F band disappears as the perturbed Mn transitions grow in. In order to obtain an order-of-magnitude concept of the oscillator-strength enhancement of Mn^{2+} caused by the presence of a next-neighbor F center, an analysis similar to that made on F_2 and F_3 centers above can be carried out. Thus, from Fig. 2(b) we equate the number of F centers lost in the annealing stage between 550 and 650 K with the number of F-center–Mn^{2+} complexes that are formed. We find for the 425-nm band which has a half-width, W_{425}, of 0.14 eV:

$$\frac{\Delta N_F f_F}{\Delta N_C f_{425}} = \frac{W_F \Delta\alpha_F}{W_{425}\Delta\alpha_{425}},$$

$$f_{425} = 0.05 f_F \quad \text{for} \quad W_{425} = 0.14 \text{ eV},$$

$$f_{328} = 0.002 f_F \quad \text{for} \quad W_{320} = 0.15 \text{ eV},$$

$$f_{600} \sim 10^{-3} f_F \quad \text{for} \quad W_{575} = 0.17 \text{ eV}.$$

A comparison of these oscillator strengths, assuming $f_F = 1$, with those for $RbMnF_3$ shown in Table I, indicates that the presence of F centers enhances the transition probability by about 10^4–10^5. Since it has been shown that super exchange in crystals containing high Mn concentrations such as $RbMnF_3$ can increase the oscillator strength by an order of magnitude[6,15] the enhancement of 10^4 is the minimum value.

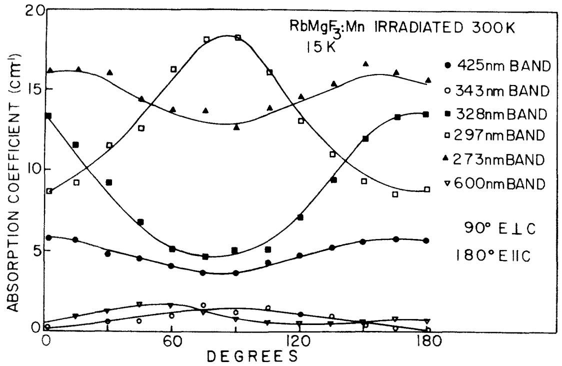

FIG. 7. Polarization dependence at 15 K of the absorption bands in the $C_{\parallel}$ $RbMgF_3$: Mn crystal electron irradiated at 300 K and heat treated to 685 K. The 90° point is when $E \perp C$ and 0° and 180° have $E \parallel C$.

The excitation spectrum for the 840-nm emission suggests that Mn^{2+} is involved in these transitions but a peak at around 600 nm is missing. This band could be due to a second type of perturbed Mn^{2+} or Fe^{3+} complex, but the origin is not clear. The emission does disappear at room temperature.

SUMMARY

It has been determined that the F-center–Mn^{2+} complex observed in $KMgF_3$ and MgF_2 also occurs in $RbMgF_3$. For the first time it has been possible to calculate the oscillator-strength enhancement due to the electron exchange between the F center and the Mn^{2+}. This increase is about 10^4–10^5 for the various transitions. Also, it is found that both the radiation production of F centers and the annealing of the radiation damage is different in pure and doped specimens. It appears that in the doped material many of the interstitials do not form large clusters but are trapped in a more statistical distribution in the lattice.

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