Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Fast luminescence observed in MnF_2 crystals

Taiju Tsuboi and P. Silfsten*
Faculty of Engineering, Kyoto Sangyo University, Kamigamo, Kyoto 603, Japan

R. Laiho
Wihuri Physical Laboratory, University of Turku, SF-20500 Turku, Finland
(Received 9 July 1990)

The luminescence lifetime in MnF_2 crystals has been investigated in a temperature range of 15–300 K using a streak camera. In addition to a long lifetime of more than 0.1 msec, which was previously observed below 40 K for a broad emission band with a peak at 582 nm, it was observed that (1) the lifetime decreases exponentially from about 30 K with increasing temperature, reaching a lifetime of 6.8 μsec at 50 K, (2) above 50 K the 582-nm emission disappears and changes to another emission band with a peak at about 570 nm, and (3) the lifetime of the 570-nm emission also decreases with increasing temperature, reaching a short lifetime of 0.5 μsec at 280 K. The origin of the 570-nm emission is discussed.

I. INTRODUCTION

A broad luminescence band with a peak around 582 nm has been observed in an antiferromagnet MnF_2 with $T_N = 68$ K.[1–3] The band appears for low temperatures (below 20 K) but decreases with increasing temperature and, it shows a peak shift toward low energy, resulting in the enhancement of a weak band with a peak at 630 nm.[3] These 582-nm and 630-nm broad bands are the multiphonon sidebands of the absorption bands due to "Mn^{2+} traps" located near impurity ions which are inevitably present, even in undoped MnF_2 crystals.[3–5] Such an impurity-induced Mn^{2+} luminescence is more intense at high temperatures than the intrinsic luminescence caused by exciton and/or exciton-magnon transitions.

The luminescence lifetime of the 582-nm band has been investigated by Holloway *et al.*[1,2] and by Flaherty and Di Bartolo.[4] The two groups found that the lifetime of the 582-nm band is almost constant below about 25 K and decreases abruptly at about 30 K, reflecting the quenching of the emission at high temperatures. A difference, however, is found between the two groups: the lifetime at 20 and 30 K was found to be about 22 and 20 msec, respectively, by Holloway *et al.*,[1] but about 38 and 3 msec by Flaherty and Di Bartolo.[5] The present work was initially undertaken to determine which value is correct.

Holloway *et al.* measured the lifetime of the 582-nm band up to 40 K,[1] while Flaherty and Di Bartolo measured up to 30 K.[5] They observed a short lifetime of about 0.15 msec at 40 K.[1] It is interesting to know what the temperature dependence is for the lifetime at high temperatures (above 40 K) because its information helps to know the origins of the 582-nm luminescence which is quenched at high temperatures. In this paper, taking into account the above questions, we investigate the lifetime of MnF_2 luminescence using a streak camera.

II. EXPERIMENTAL PROCEDURE AND EXPERIMENTAL RESULTS

A single crystal of MnF_2 used in the present experiment was grown at Optovac Co. Its size was $11.45 \times 11.45 \times 9.71$ mm. A Molectron UV14 N_2 laser was used as an excitation light source. The pulse width is 10 nsec and the peak power is 425 kW. The crystal luminescence was collimated, from the direction perpendicular to the exciting light, to an entrance slit of a Jobin-Yvon HR 320 polychromator and detected by a Hamamatsu Photonics C2830 Streak Camera equipped with a Hamamatsu Photonics C3140 Peltier-element-cooled charge-coupled device (CCD) photodetector. The CCD camera can detect a very weak luminescence. It was possible to synchronize the laser pulse with the streak sweep within the jitter of less than 2 nsec. The luminescence decay and time-resolved spectrum were obtained using a Hamamatsu Photonics Temporal Analysis computer system.

Figure 1 shows an absorption spectrum of MnF_2 at 300 K. Several absorption bands due to Mn^{2+} ions, called *A*, *B*, *C*, . . . , are observed in the high-energy region from 550 nm. The N_2 laser emitting a 337.1-nm light excites

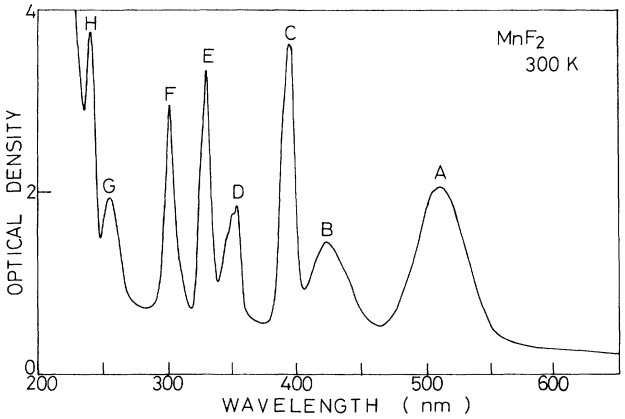

FIG. 1. Absorption spectrum of a MnF_2 crystal at 300 K.

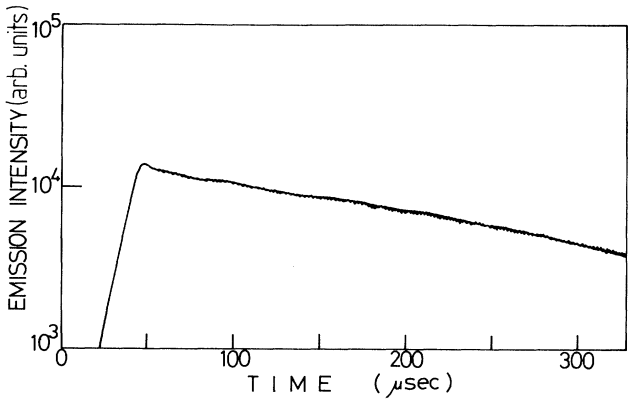

FIG. 3. Decay process in a semilog plot for the 582-nm emission band at 35.5 K.

the E absorption band. A typical luminescence spectrum is shown in Fig. 2 where a luminescence detected at 33 msec after the laser pulse excitation is drawn. A broad band with a peak around 582 nm is observed at 20 K and a weak band is found around 630 nm, in agreement with the previous result.[5] The same spectrum was also obtained in a 0.1-μsec delay after the pulse excitation. No difference was found in the time-resolved luminescence spectra measured at various delay times between 15 nsec and 50 msec. The same was true for the spectra measured between 15 and 290 K.

A single luminescence decay curve was observed in the semilog plot. A typical decay curve is shown in Fig. 3. In Fig. 4 the lifetime is plotted against temperature. The lifetime has a tendency to be constant below 20 K and decreases exponentially above about 20 K as previously observed.[1,5] However, it is observed to deviate from the exponential line above 50 K. No definite anomaly was observed at Néel temperature ($T_N = 68$ K).

We find a luminescence lifetime of 35 msec at 20 K and 1.6 msec at 30 K. These values are closer to the ones of Flaherty and Di Bartolo[5] than Holloway *et al.*[1] Furthermore, the thermal behavior of lifetime observed by us is quite similar to the result of Flaherty and Di Bartolo who measured in a temperature range below 30 K.

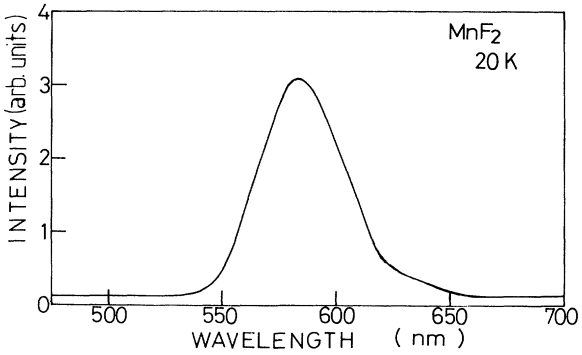

FIG. 2. Time-resolved luminescence measured for 70 μsec at 33 msec after N_2 laser pulse excitation at 20 K.

III. DISCUSSION

The impurity-induced Mn^{2+} luminescence is produced by "activation-type" processes and therefore it has a temperature dependence of lifetime described by the form

$$\tau^{-1} = \tau_F^{-1} + \tau_N^{-1} \exp(-\Delta E/kT) , \quad (1)$$

where τ_F is the radiative lifetime, τ_N is the nonradiative lifetime, and ΔE is the activation energy which corre-

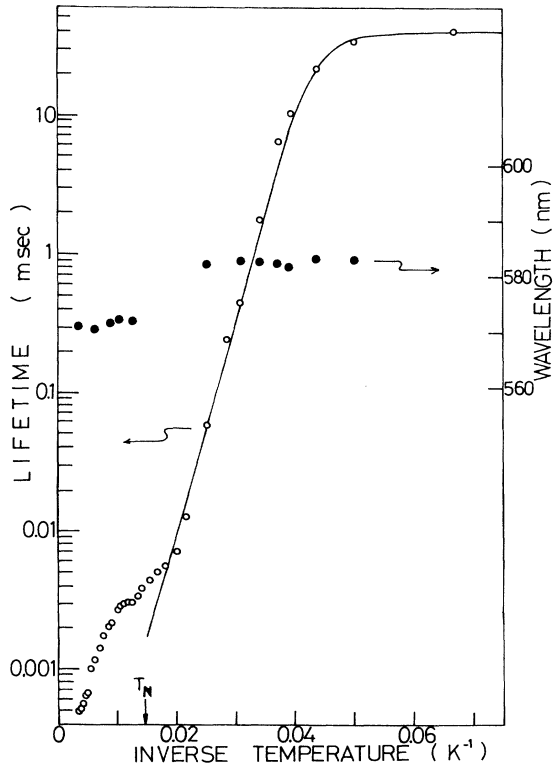

FIG. 4. Variation of the luminescence lifetime (open circle) of MnF_2 with temperature. The peak position (solid circle) of luminescence band is also plotted against temperature.

sponds to the energy separation between the lowest edge of the A absorption band and the upper edge of the 582-nm emission band.[3,4,6,7] The 582-nm emission is also found to obey the form (1).

The lifetime of the 582-nm emission decreases exponentially from 26 to 50 K but deviates from the exponential line above 50 K. A good fitting of the lifetime data with the curve of form (1) is obtained when we choose $\tau_F = 39.2$ msec, $\tau_N = 5.44$ nsec, and $\Delta E = 256.3$ cm^{-1} for the 582-nm emission (see a solid line in Fig. 4). It was observed that the luminescence at high temperatures (above 90 K) has a peak position around 570 nm[8] (see Fig. 4).[8] Therefore, the deviation from the exponential line is understood to arise from the appearance of new luminescence from a Mn trap which is different from the Mn trap responsible for the 582-nm luminescence. It is noted that the deviation from the form (1) occurs not at T_N but near T_N. This suggests that the crystal symmetry around Mn^{2+} ion is changed by a magnetostriction accompanied by the magnetic phase transition, resulting in a formation of such a new Mn^{2+} trap above around T_N.

Luminescence with a long lifetime of more than 1 msec have been reported in various Mn^{2+}-compound magnetic crystals (see, e.g., Refs. 3, 4, 9 and 10). The 570-nm emission was found, by the present investigation, to produce a short lifetime of less than 8 μsec, e.g., 485 nsec at 280 K. Such a fast decay was observed in MnF_2 for the first time. According to Goldberg *et al.*,[3] the greater an emitting level is perturbed by the trap, the shorter is its radiative lifetime. Therefore the 570-nm emission is suggested to be caused by a Mn^{2+} ion strongly coupled with the trap.

The following explanation appears to be possible for the 570-nm emission. The 582-nm emission is dominant at low temperatures but is quenched at high temperatures. As the temperature is raised, the shallow Mn traps responsible for the 582-nm emission cannot retain the excitation energy and begin to lose their excitation by "*boil-back*" to the Mn exciton band. At this point, the excitation propagates freely throughout the crystal, and it is eventually transferred to the deeper Mn traps which are present in the paramagnetic phase. As the result, the 570-nm emission occurs.

ACKNOWLEDGMENTS

The present work was supported by a Grant-in-Aid from the Japanese Ministry of Education and Science. One of the authors (P.S.) thanks the Academy of Finland for financial support, which enabled him to work at Kyoto Sangyo University, Japan.

---

*Permanent address: University of Joensuu, Joensuu, Finland.

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

[2]W. W. Holloway and M. Kestigian, Phys. Rev. Lett. **13**, 235 (1964).

[3]V. Goldberg, R. Moncorge, D. Pacheo, and B. Di Bartolo, in *Luminescence of Inorganic Solids,* edited by B. D. Bartolo (Plenum, New York, 1978), p. 603; G. F. Imbush, *ibid.*, p. 155.

[4]J. Danko, D. Pacheo, and B. Di Bartolo, J. Lumin. **28**, 27 (1983); Phys. Rev. B **28**, 2382 (1983); B. Di Bartolo, J. Danko, and D. Pacheo, *ibid.* **35**, 6386 (1987).

[5]J. M. Flaherty and B. Di Bartolo, Phys. Rev. B **8**, 5232 (1973).

[6]R. L. Greene, D. D. Sell, R. S. Feigelson, G. F. Imbusch, and H. J. Guggenheim, Phys. Rev. **171**, 600 (1968).

[7]B. A. Wilson, W. M. Yen, J. Hagarty, and G. F. Imbusch, Phys. Rev. B **19**, 4238 (1979).

[8]The peak position was obtained by a time-resolved luminescence technique using a streak sweep time of 0.1 msec after laser excitation.

[9]E. Strauss, V. Gerhardt, and W. Gebhardt, J. Lumin. **18/19**, 151 (1979).

[10]N. Koumvakalis, W. A. Sibley, and G. E. Venikouas, J. Lumin. **15**, 283 (1977).