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Spin-wave-assisted photoluminescence in MnS

Shōsuke Mochizuki
Department of Physics, College of Humanities and Sciences, Nihon University, 3-25-40 Sakurajosui, Setagaya-ku, Tokyo 156, Japan

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Abstract. We report the observation of the photoluminescence in antiferromagnetic MnS. A strong emission band centred at 1.43 eV is observed at 78 K in MnS powder. The Stokes shift from the lowest 3d crystal-field absorption peak is at least 0.6 eV. The temperature dependences of the emission peak energy, the integrated intensity and the decay curve of the photoluminescence are measured at various temperatures from 78 to 200 K. The results are interpreted qualitatively by a model in which the emission originates from the impurity- and defect-perturbed Mn^{2+} excitons by taking into account the spin ordering of Mn^{2+} ions.

1. Introduction

In this paper, we report the measurements of the photoluminescence spectra, the excitation spectra and the decay curves of MnS as a function of temperature in both its antiferromagnetic and its paramagnetic phases.

Spin-wave-assisted photoluminescence in some manganese compounds—MnF_2 (Holloway *et al* 1965, Greene *et al* 1968), alkali manganese trifluorides (Holloway *et al* 1964, 1965) and $MnCO_3$ (Komura *et al* 1985)—have been reported already. These photoluminescence studies give information on the 3d electronic structure and on the spin ordering of Mn^{2+} ions. MnO and MnS are simplest of all manganese compounds and their physical properties have been studied thoroughly. Recently, we have observed spin-wave-assisted photoluminescence in MnO (Mochizuki *et al* 1990) for the first time. We have explained the results by the photon emission due to the destruction of the photo-excited Mn^{2+} excitons accompanied by simultaneous creation and destruction of two kinds of the spin-wave excitation; so the energy and momentum are conserved.

MnS is an ionic crystal with the face-centred cubic structure above the Néel temperature T_N (152 K) and the crystal transforms to an antiferromagnetic structure which is slightly distorted from the ideal NaCl structure. In both phases, there are several intense absorption bands in the visible and near-ultraviolet regions due to the crystal-field transitions of the Mn^{2+} ions (Huffman and Wild 1967). Although these transitions are strictly forbidden owing to the spin and parity selection rules, the observed bands have considerable oscillator strength. In order to interpret these intense absorption bands, various models for the absorption mechanism have been proposed such as

(i) the phonon perturbation model,
(ii) the spin–orbit interaction model and
(iii) magnon-sideband absorption model (Motizuki and Harada 1970).

In model (iii), the spin-wave excitation breaks the inversion symmetry and causes the electric-dipole magnon sidebands. The magnon sideband absorption arises from the simultaneous creation of an Mn^{2+} exciton and magnon.

The results presented in this paper are from an integrated set of the measurements made to determine the photo-responses of MnS. So far as we know, no study has been reported on the photoluminescence in MnS.

2. Experimental details

Although MnS single crystals can be obtained by the chemical transport method with iodine as the carrier, in order to avoid some impurity effects due to the remaining iodine and other impurities, we used MnS powder coated by non-fluorescent varnish, and pressed MnS powder. The MnS powder contains Si (0.009%), Ni (0.003%), Ca (0.001%), Cu (0.001%), Ag (less than 0.001%) and Mg (less than 0.001%). X-ray diffractometry has indicated that the MnS powder used to be NaCl-type single phase, and no other diffraction peak due to β-MnS, γ-MnS and MnO was detected. Since the pressed MnS powder specimen shows more intense emission and is not affected by pressing, we studied mainly the pressed MnS powder. Such a specimen is prepared by pressing the MnS powder under a pressure of 200 kgf cm^{-2} for 30 min at room temperature. This specimen was mounted on the cold finger of a liquid-nitrogen cryostat.

The emission spectra were obtained using a Xe-arc lamp with a monochromatic system as the excitation source and a monochromator (Jobin–Yvon H-20 IR) with a germanium detector (North Coast Scientific Corporation EO-817L).

The excitation spectra were obtained using the Xe-arc lamp with a monochromator (Jobin–Yvon H-20 UV) as the excitation source and the above-mentioned monochromator and germanium detector as the observation system.

The decay curves were obtained using a dye laser excited by an N_2 laser (PRA LD-2C and LN-120C), and the above-mentioned monochromator (Jobin–Yvon H-20 IR), a photomultiplier (Hamamatsu R316-02) and a digital oscilloscope (Hitachi VC-6165) were used as the observation system. The half-width of the laser pulse was about 300 ps and the total response time of the observation system was less than 1 μs.

In the emission and excitation spectra measurements, the intensity of the excitation beam was modulated by a mechanical chopper (NF CH-352), and the luminescence signal was measured with a lock-in amplifier (NF LI-570). The spectral response of the optical system including the focusing lenses and mirrors was carefully measured using a calibrated source and used to correct the raw data.

3. Results

Huffman and Wild (1967) have reported three absorption bands at about 2.08, 2.46 and 2.78 eV and they have assigned them to the 3d crystal-field splitting transitions from the ground state $^6A_{1g}$ to the excited states ${}^4_{a}T_{1g}$, ${}^4_{a}T_{2g}$ and ${}^4_{a}A_{1g}$: ${}^4_{a}E_g$, respectively. At 78 K, we excited the MnS specimen by radiation of these energies and observed intense emission. The emission decreased with increasing temperature. A typical result is shown

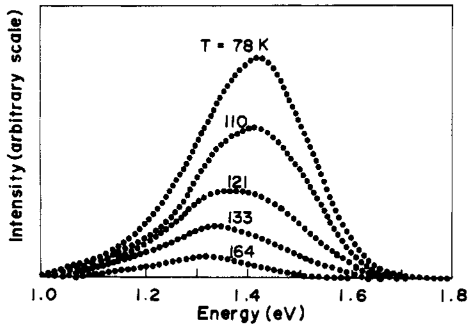

Figure 1. Photoluminescence spectra of MnS.

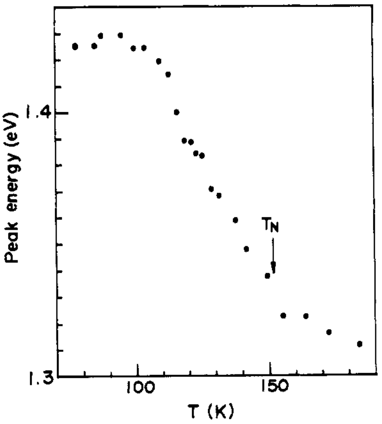

Figure 2. Temperature dependence of the emission peak energy of MnS.

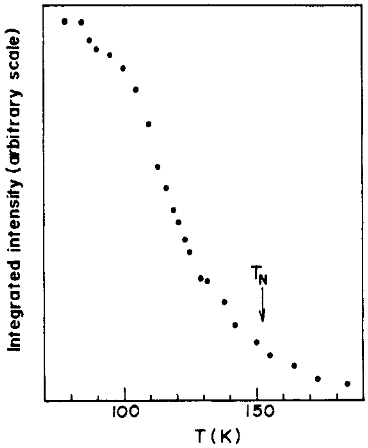

Figure 3. Temperature dependence of the integrated emission intensity of MnS.

in figure 1. As seen in this figure, a broad emission band appears at 1.43 eV and the Stokes shift from the $^6A_{1g}$–$^4_aT_{1g}$ peak is about 0.6 eV, which is higher than those of other manganese compounds. With increasing temperature from 78 K, the peak energy of the emission band decreases and the integrated intensity also decreases. The temperature dependences of the peak energy and the integrated intensity are shown in figures 2 and 3, respectively. These temperature dependences are very similar to that of the shift of the $^6A_{1g}$–$^4_aT_{1g}$ absorption peak in MnS reported by Huffman and Wild (1967). The shift of the peak was attributed to the effect of magnetic ordering. Moreover, the temperature dependence of the integrated intensity is similar to that of the 1.25 eV band in MnO. These features indicate that the photoluminescence observed in MnS is closely related to the magnetic ordering of Mn^{2+} spins. By the way, it is found that the above-mentioned results do not depend on the excitation energy. This indicates that the observed emissions do not come from the Mn^{2+} exciton band but other electronic levels (band) and that such electronic levels (band) can be populated by the upper Mn^{2+} excited levels.

Using the same specimen, we studied the following excitation spectra at 78 K: the emission peak (1.43 eV), the higher-energy side of the peak (1.55 eV) and the lower-energy side of the peak (1.31 eV). The results are shown in figure 4. A comparison of these excitation spectra with the optical absorption spectra reported by Huffman and Wild (1967) indicates that the excitation efficiency peaks observed at about 2.06, 2.46 and 2.76 eV correspond to the crystal-field absorption peaks of Mn^{2+} ions in the cubic

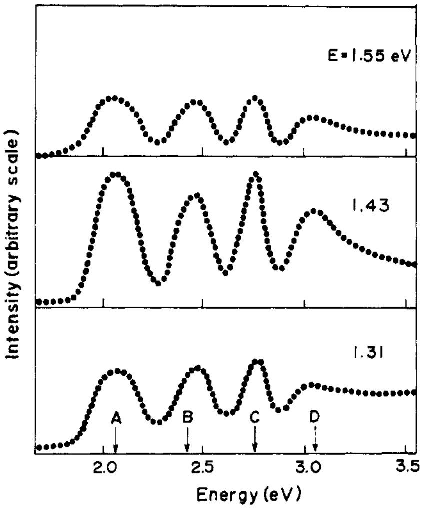

Figure 4. Excitation spectra of MnS at 78 K.

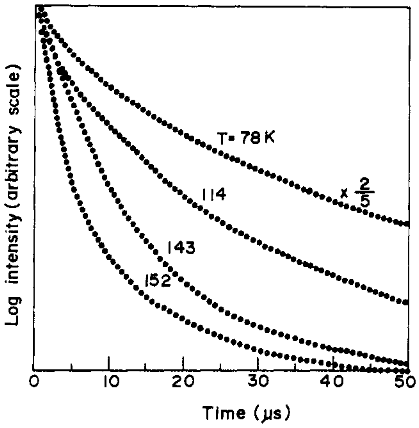

Figure 5. Decay curves of the emission of MnS.

field, which were labelled A, B and C, respectively, by Huffman and Wild (1967); the energies corresponding to these absorption peaks are indicated by arrows in this figure. Such good correspondence and the emission spectra independent of excitation energy, apart from the emission intensity, indicate that the emission levels (band) are populated by the upper Mn^{2+} excited levels. The emission band observed at about 3.04 eV does not correspond clearly to the absorption band. Although the absorption peaks observed at 2.96 and 3.05 eV at 4.2 K are assigned to the spin–orbit-split exciton peak associated with the transition from the broad 3p band to narrow 3d band, there is some possibility of the 3d crystal-field splitting transitions, the ${}^6A_{1g}$–${}^4_bT_{2g}$ transition and the combinations of three kinds of elementary excitation (i.e. exciton, magnon and phonon). However, it is known that the surface defects reduce the efficiency of the photoluminescence in the high-absorption region; this will induce a spurious emission peak. At the present stage, we have no other information with respect to band D.

In order to study the structure of the above-mentioned broad emission band, we measured the transient properties of the photoluminescence of the same specimen at various energies in the temperature range from 78 to 200 K. In figure 5, typical decay curves are shown for several temperatures. The observations were made at the respective emission peak energies. As shown in this figure, the decay curves are not single exponential and are not a simple power of the time elapsed after the excitation. These decay curves are scarcely dependent on the excitation energy up to 50 μs. Non-exponential behaviour should be observed as a consequence of the non-exponential nature of the fluorescent level (band) decay. Although the decay curves are exponential, we tried to deduce the average lifetime from the faster part (2.5–10 μs) at various temperatures. The result is shown in figure 6. This behaviour is similar to those of the peak energy and the integrated intensity. This indicates that the lifetimes of the fluorescent levels (band) are affected by the magnetic ordering of Mn^{2+} spins. Moreover, we compared the emission spectrum at 2.5 μs after the excitation with that measured under continuous illumination, as shown in figure 7. These spectra were measured at 78 K by exciting electrons from the ${}^6A_{1g}$ state to the ${}^4_aT_{2g}$ state. The full curve and the broken curve

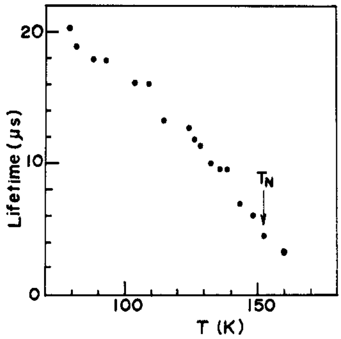

Figure 6. Temperature dependence of the lifetime of MnS.

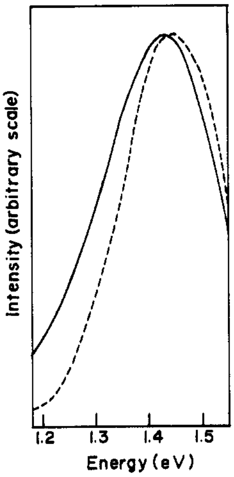

Figure 7. Time-resolved emission spectra of MnS at 78 K. The full curve corresponds to the emission spectrum at steady state and the broken curve corresponds to that at 2.5 μs after excitation.

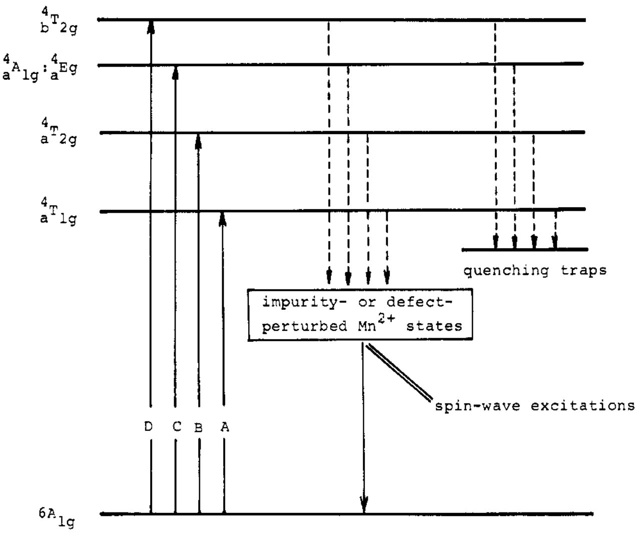

Figure 8. Electron energy scheme for the photoluminescence of MnS. The upward full arrows indicate the absorption, the downward full arrow indicates the radiative transition, the downward broken arrows indicate the non-radiative transitions, and the parallel line indicates the participation in the transition.

represent the emission spectra at steady state and at 2.5 μs, respectively. As seen in this figure, the decay time increases with increasing time and with decreasing emission energy. This typically indicates that the emission band comes from many electronic levels, as observed for MnO (Mochizuki *et al* 1990).

4. Discussion

The present experimental results on the photoluminescence of MnS may be summarised as follows.

(i) The photoexcitations from the sextet ground state to the quartet excited states of Mn^{2+} ions in an MnS crystal induce a broad-band emission at about 1.43 eV with a large Stokes shift.

(ii) The observed emission spectra do not depend on the excitation photon energy, apart from the intensity.

(iii) The decay times of the luminescence increases with increasing time and decreasing emission energy.

(iv) The temperature dependences of the peak energy, the integrated intensity and the decay time of the emission are similar to that of the shift of the ${}^6A_{1g}$–${}_a^4T_{1g}$ absorption peak; the peak shift was attributed to the effect of the magnetic ordering.

The result (iv) suggests that the luminescent centres are closely related to the magnetic ordering of the Mn^{2+} spins in an MnS crystal.

In order to explain the photoluminescent properties of manganese compounds, some attempts have been made by assuming the existence of impurity-perturbed Mn^{2+} states (Greene *et al* 1968) or by using the configurational coordinate curves affected by the degree of the spin alignment (Holloway *et al* 1965). Although it is not easy to confirm their validity at the present stage, our results can be interpreted using these models. Before discussing our results, we should mention the character of real MnS. It is known that MnS contains a small quantity of oxygen impurities and slightly deviates from the stoichiometric composition. Under such circumstances, different kinds of extrinsic fluorescent centres and different types of trap level may be formed. Moreover, some of Mn^{2+} ions may be perturbed by such surrounding impurities and crystalline defects. Then, the excited energy levels of the Mn^{2+} ions which have been thus perturbed may be shifted to lower energies (Greene *et al* 1968), thereby creating traps for the freely propagating intrinsic Mn^{2+} excitons. This may induce a Stokes shift in the photoluminescence and the independence of the photoluminescence spectrum with respect to the excitation energy, apart from the intensity, which has already been ascertained in the present experiments. Since there are various types of perturbation, the excited energy levels of the perturbed Mn^{2+} ions make up a band and thus we may observe an emission band in which the levels have different lifetimes. These are also observed in the present experiments as shown in figures 1, 4 and 7. It should be pointed out that these perturbed Mn^{2+} levels may correspond to the long-lived fluorescent states proposed by Holloway *et al* (1965), because we cannot detect intrinsic emission from the unperturbed Mn^{2+} states.

Generally speaking, the optical absorptions of antiferromagnetic manganese compounds are accompanied by the creation of Mn^{2+} excitons and, simultaneously, by the creation and destruction of spin-wave excitations, and thus the excited states created are destroyed by the creation of photons and, simultaneously, by the creation and destruction of spin-wave excitations; so the energy and momentum are conserved. Thus, since the photoluminescence of MnS is the excitonic transition accompanied by spin-wave excitations, the emission intensity is strongly dependent on the spin ordering in MnS. According to the magnetic specific-heat data (Huffman and Wild 1966, 1967) of MnS, the short-range magnetic ordering of Mn^{2+} spins seems to remain above the Néel temperature and then the change in the spin-wave property does not occur abruptly at the Néel temperature. This is the reason why the temperature dependence of the integrated emission intensity of MnS is sluggish near the Néel temperature, as shown in figure 3. In this discussion, it was assumed that the temperature dependence of the exchange integral is not changed considerably by the perturbation.

The energy of the *i*th perturbed Mn^{2+} ion may be reduced as a result of the antiferromagnetic ordering by

$$-2S_i \sum_j J_{ij} S_j = E_{ij} \tag{1}$$

where S_i is the spin angular momentum of the *i*th perturbed ion, J_{ij} is the exchange constant between the *i*th ion and the *j*th ion which is perturbed or not perturbed, and S_j is the spin angular momentum of the *j*th ion. The emission energy depends on E_{ij}. This E_{ij} will decrease with increasing temperature, as shown in figure 2.

Although the above discussions are very simple, if we add the idea of the magnetic local model affected by lattice distortions, the discussions may be translated to the model proposed by Holloway *et al* (1965).

Finally, on the basis of the above discussion, we propose the electronic energy scheme for the photoluminescence of MnS in figure 8. As illustrated in this figure, the optical absorptions produce the quartet excited states of Mn^{2+} ions, the intrinsic Mn^{2+} excitons, and then the excitons decay after a certain time through the following non-radiative processes:

(i) transition to some quenching trap levels;

(ii) the transition to some impurity- or crystalline-defect-perturbed Mn^{2+} states (band).

The luminescent transitions from these perturbed Mn^{2+} states (band) to ground state are achieved by creation and destruction of spin-wave excitations so as to conserve the energy and the momentum. Although the absorption and emission peaks at about 3 eV can be assigned to different transitions, we assumed that this transition is the ${}^6A_{1g}$–${}^4_bT_{2g}$ transition.

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