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Spin-wave-assisted photoluminescence in MnS at low temperatures

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Abstract. The temperature dependence of the spin-wave-assisted photoluminescence in MnS has been studied at low temperatures down to 5 K. Below 50 K, a new strong emission band centred at 1.64 eV appears in accordance with the vanishing of the emission band (centred below 1.43 eV) observed in our previous experiments. The results obtained in both our present and our previous studies are discussed using the impurity-perturbed Mn^{2+} exciton model or the self-trapped Mn^{2+} exciton model.

1. Introduction

Very recently, we have reported the photoluminescence properties of the cubic anti-ferromagnets MnO (Mochizuki *et al* 1990) and MnS (Mochizuki 1990) above liquid-nitrogen temperature. For MnO, two strong broad emission bands centred at 1.66 and 1.25 eV with large Stokes shifts were observed below the Néel temperature T_N and competition between the intensities of these bands was also observed while, for MnS, only a strong broad emission band centred at 1.43 eV with a large Stokes shift was observed. These results were qualitatively interpreted using a model in which the emission originates from the spin-wave-assisted decay of the impurity-perturbed Mn^{2+} excitons. Prohofsky (1965) has already proposed a model to explain the photoluminescence properties (temperature dependences of the emission intensity, peak frequency and lifetime) of antiferromagnetic manganese compounds. In his model, a coupling of the lattice distortion with the magnetic interaction of the photo-excited Mn^{2+} ions produces the magnetic virtual local mode centred about them and then causes rapid condensation of the local mode below $\frac{1}{2}T_N$. Now in order to examine these proposed models and other theoretical predictions of the motion of the Mn^{2+} excitons (Ueda and Tanabe 1980), we need to extend the photoluminescence measurements to a lower-temperature region. In this paper, we report the measurement of the photoluminescence spectra of MnS in the temperature range from 5 to 180 K, together with some discussion.

2. Experimental details

The measurements were made using the compacted MnS powder, i.e. the same specimen as used in the previous experiments. The MnS powder contains Si (0.009%), Ni

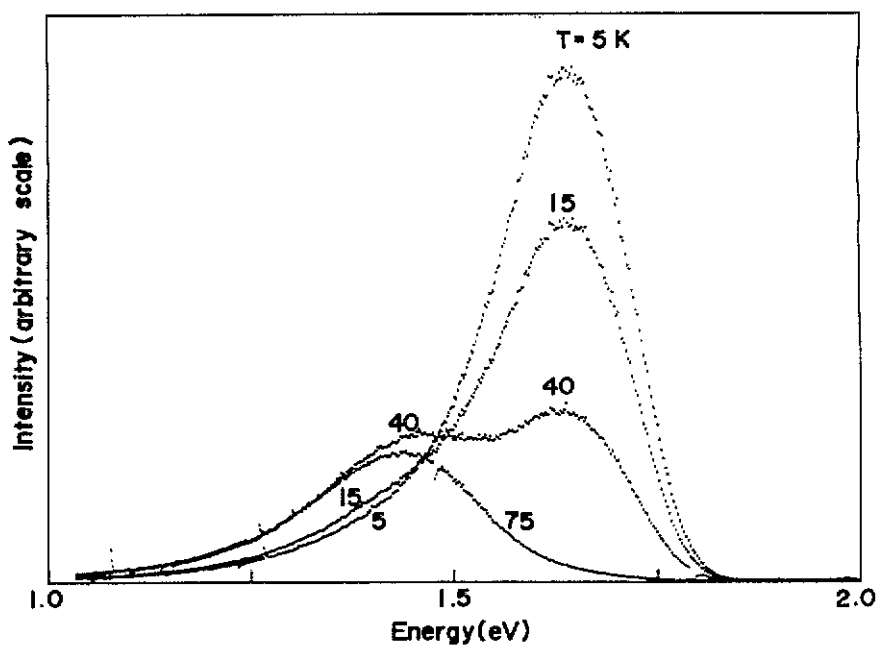


Figure 1. Photoluminescence spectra of MnS at various temperatures ($T = 5, 15, 40$ and 75 K).

(0.003%), Ca (0.001%), Cu (0.001%), Ag (less than 0.001%) and Mg (less than 0.001%) and is NaCl-type single phase. An Ar laser (wavelength, 488.0 nm) was used to excite the emission. Temperature variation was achieved using a He-gas-flow-type cryostat. The emission spectra were obtained using a grating monochromator (Jobin-Yvon H-20 IR) with a germanium detector (North Coast Scientific Corporation EO-817L). The experimental details have already been reported in the previous paper (Mochizuki 1990).

3. Results

Figure 1 shows the photoluminescence spectrum of MnS as a function of temperature. As shown in this figure, at 5 K, only a strong broad asymmetrical band (A-band emission) is observed at 1.64 eV. The Stokes shift from the lowest crystal-field absorption peak is at least 0.43 eV, which is close to that for MnO (Mochizuki *et al* 1990). On increasing the temperature, the emission intensity of the A band decreases in the higher-energy region above 1.46 eV, while the intensity below 1.46 eV increases. The peak energy of the A band is independent of temperature. At 40 K, we can clearly recognize another emission band (B-band emission) centred at 1.44 eV; this B band is simply the band observed in previous experiments above liquid-nitrogen temperature (Mochizuki 1990). On further increasing the temperature, the intensity of the B band begins to increase, while the intensity of the A band decreases rapidly and then, at 65 K, the A band disappears completely. After the emission intensity of the B band has reached a maximum value at 50 K, it decreases with increasing temperature. The peak energy of the B band also decreases with increasing temperature as reported in the previous paper (Mochizuki 1990).

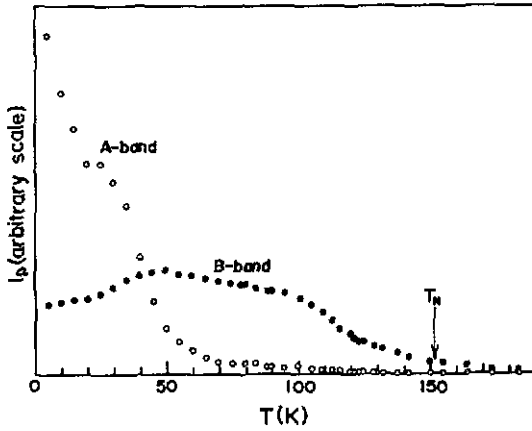


Figure 2. Temperature dependences of the peak intensity I_p for the A-band and B-band emissions. For the temperature range (above 50 K) in which the A band is incorporated in the B band, the intensity at 1.64 eV is plotted for the A band. In a similar manner, below 40 K, I_p at 1.44 eV is plotted for the B band.

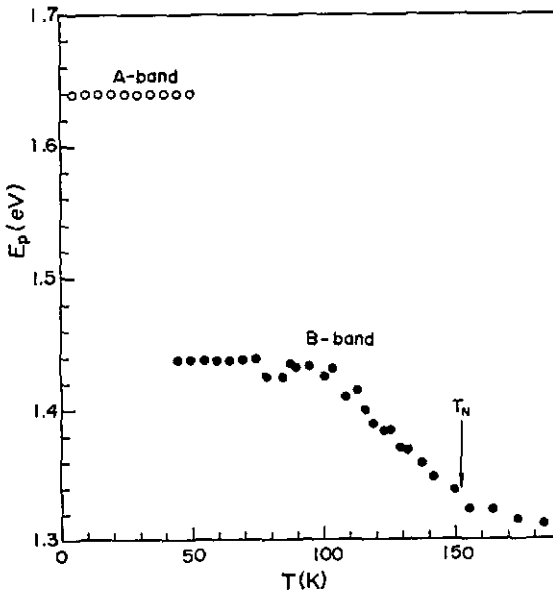


Figure 3. Temperature dependences of the emission peak energy E_p for the A and B bands.

The temperature dependences of the intensities I_p at 1.64 eV, corresponding to the peak energy E_p of the A band, and at the peak energy of the B band, are shown in figure 2. Figure 3 shows the temperature dependences of the peak energies of the A and B bands. Since the A band disappears above 65 K and the B band is incorporated in the A band below 40 K, the dependences are shown in the restricted temperature ranges.

4. Discussion

Both the present and the previous experimental results (Mochizuki 1990) on the photoluminescence of MnS may be summarized as follows.

(i) The photo-excitations from the sextet ground state of the Mn^{2+} ions in MnS induce two broad-band emissions at about 1.64 and 1.44 eV with large Stokes shifts.

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

(iii) The decay times of the luminescence increase with increasing time elapsed after excitation and with decreasing emission energy.

(iv) The A band exists only below 65 K (about $0.43T_N$). Although the peak energy does not depend on temperature, the intensity increases markedly with decreasing temperature. Competition between the intensities of the A and B bands is clearly observed.

(v) The temperature dependence of the peak energy of the B band is similar to that of the shift of the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ absorption peak; the peak shift was attributed to the effect of the magnetic ordering of Mn^{2+} (Huffman and Wild 1966).

(vi) The photoluminescence spectrum of MnS is very similar to that of MnO (Mochizuki *et al* 1990). Very recently, we have found magnon side bands on the higher-energy side of the A band of MnO (Mochizuki *et al* 1991).

The results (iv)–(vi) indicate that the luminescent centres are closely related to the magnetic ordering of Mn^{2+} spins in MnS . The results (ii) and (iii) indicate that the luminescent energy levels (bands) are populated by the upper-lying Mn^{2+} excited levels and that these bands consist of many kinds of levels with different decay times. The result (iv) indicates that the observed emission intensity competition arises from some phonon-assisted energy transfer or from thermal-magnon-assisted energy transfer from the luminescent centre of the A-band emission to that of the B-band emission.

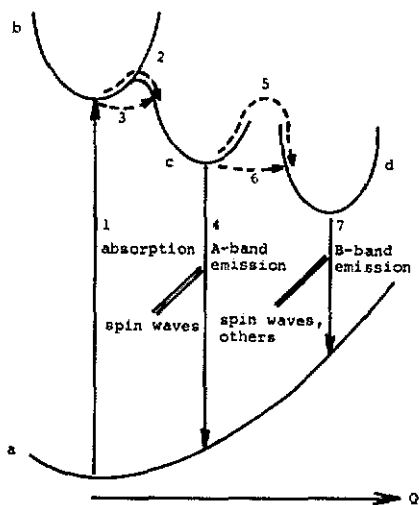


Figure 4. Configuration diagram for the radiative decay of a self-trapped Mn^{2+} exciton in MnS .

In order to determine whether the above-mentioned photoluminescence with large Stokes shift arises from the decay of intrinsic self-trapped Mn^{2+} excitons or from the decay of impurity-perturbed Mn^{2+} excitons, we attempted to increase the specimen purity and the crystalline quality. At the present stage, however, our experimental results lead us to suggest the energy schemes given in figures 4 and 5 for the photoluminescence in

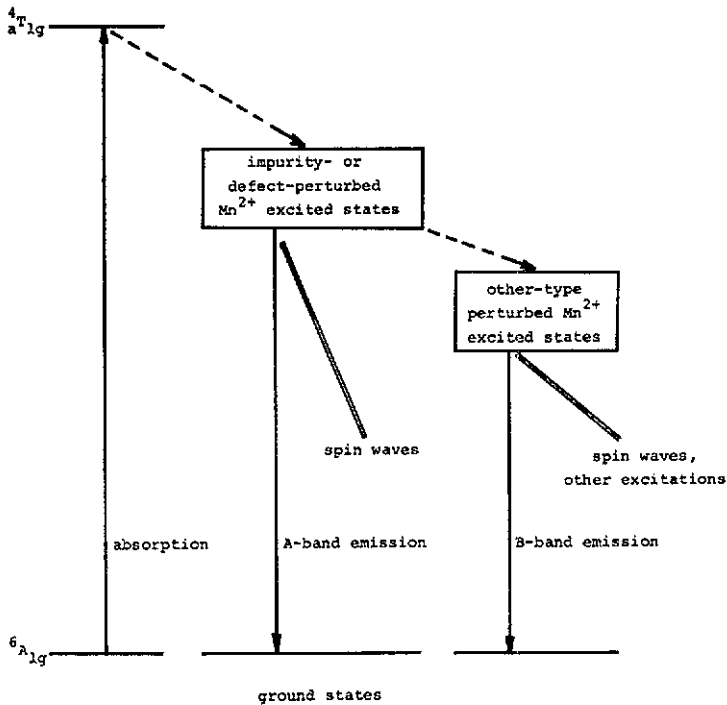


Figure 5. Electron energy scheme for the radiative decay of an impurity-perturbed Mn^{2+} exciton in MnS.

MnS. In the figures, for simplification, the transitions involving higher excited states (${}^4T_{2g}$, ${}^4A_{1g}$, 4E_g , etc) of Mn^{2+} are omitted.

Figure 4 represents the photoluminescence process based on the decay of the self-trapped Mn^{2+} excitons; this is quite analogous to the model proposed by Prohofsky (1965). In this figure, the curves a, b, c and d represent the ground state of Mn^{2+} ions, the Mn^{2+} exciton band, the long-lived luminescent self-trapped state of Mn^{2+} exciton and the other trap state, respectively. The curvature, distortion and energy value of curve c depend on the magnetoelastic interaction and the spin alignment of the excited Mn^{2+} ions. The transitions are indicated by the lines 1–7. Optical absorption (line 1) produces Frenkel-type Mn^{2+} excitons and then the Mn^{2+} excitons are self-trapped by an interaction between the local lattice distortion due to the reduced number of the e_g orbitals and the magnetic alignment of Mn^{2+} spins, which produces the local modes. The relaxation to the self-trapped state is achieved by the phonon-assisted process (line 2) or by the tunnelling process (line 3). At low temperatures, most of the self-trapped Mn^{2+} excitons decay radiatively by the simultaneous or subsequent emission of spin-wave excitations and phonons, as indicated by line 4, and a small number of them decay into the other trapped state d by the phonon-assisted process (line 5) or the tunnelling process (line 6). Such decays produce a strong emission band accompanied by a weak shoulder on the lower-energy side as observed at 5 K. On increasing the temperature, the above-mentioned phonon-assisted process (line 5), namely the energy transfer from state c to state d, and the local modes are thermally activated, which reduces the degree of the spin alignment of the luminescent Mn^{2+} ions. These may induce a considerable decrease in the radiative transition (line 4, A-band emission) as shown in figure 2 and

deformations of the energy curves c and d, while the radiative transition (line 7) from the other trapped state increases with increasing temperature; this produces the second emission band at low energies, which corresponds to the observed B-band emission. Since the observed peak shift of the B band is closely related to the magnetic ordering in MnS as the result (iv), the trap state is connected to the Mn^{2+} states perturbed by impurities (other kinds of atom or ion, non-stoichiometry, and crystalline defects). The decays of such states are accompanied by spin-wave excitations and other types of excitation (magnetic excitations due to short-range spin ordering and phonons).

Figure 5 represents the photoluminescence process assuming the existence of impurity-perturbed Mn^{2+} luminescent centres; this is quite analogous to the proposals in our previous papers (Mochizuki *et al* 1990, Mochizuki 1990). As illustrated in this figure, the optical absorption produces Frenkel-type Mn^{2+} excitons and then decays after a certain time through the following non-radiative process:

- (1) transition to some impurity- or crystalline-defect-perturbed Mn^{2+} states or
- (2) transition to some quenching trap states.

The luminescent transitions from these perturbed Mn^{2+} states to the ground state are achieved by the creation and destruction of spin-wave excitations or other types of excitation (magnetic excitations due to short-range spin ordering and phonons) so as to conserve the energy and momentum. Moreover, the result (iii) indicates that each luminescent level has a different lifetime and that the energy transfers between such levels can cover many perturbed Mn^{2+} ions.

Acknowledgments

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