Spin-wave-assisted photoluminescence in MnO at low temperatures

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Abstract. The temperature dependences of the peak energies and intensities of the high-energy band (band A) and the low-energy band (band B) of the spin-wave-assisted photoluminescence in MnO have been studied at low temperatures down to 5 K. Side bands due to combinations of the elementary excitations (Mn^{2+} excitons, spin-wave quanta (magnons), TO phonons and LO phonons) were also observed below 40 K as shoulders appearing on the high-energy side of band A.

1. Introduction

The photoluminescence properties of MnO and MnS have great potential in helping us to understand the optical excitation process, optical relaxation and excitation transfer in magnetically ordered systems because MnO and MnS have simple magnetic structures. Very recently, we have reported the photoluminescence properties of MnO (Mochizuki *et al* 1990) and MnS (Mochizuki 1990, Mochizuki and Takayama 1991). For both these antiferromagnets, two strong emission bands with large Stokes shifts were observed; the high-energy emission band (band A) for both MnO and MnS vanishes above the corresponding Néel temperature T_N (118 K for MnO and 152 K for MnS) while the low-energy emission band (band B) persists in the paramagnetic phases of both MnO and MnS. These results were qualitatively interpreted as the magnetic-excitation(long- and short-wavelength spin waves)-assisted decays of the impurity-perturbed Mn^{2+} excitons or of the intrinsic Mn^{2+} excitons self-trapped around the local distortion both owing to the reduced number of the electrons in the e_g orbitals and owing to the reduced magnetic alignment of Mn^{2+} spins for photo-excited ions ($s = \pm\frac{5}{2} \rightarrow \pm\frac{3}{2}$). In order to examine these models, we should study the photoluminescence spectra in a wide temperature range and find the magnon side bands, together with the time evolution of the photoluminescence spectra. Since our previous measurements for MnO were limited to temperatures above 77 K, we have

recently extended the measurements of the photoluminescence spectra at low temperatures down to 5 K. In the present paper, we report the temperature dependence of the photoluminescence spectra of MnO above 5 K and the side bands due to combinations of Mn^{2+} excitons, magnons, TO phonons and LO phonons. The results of the dynamic measurements on MnO and MnS are now progressing in our laboratory and will appear in a separate paper (Mochizuki *et al* 1992).

2. Experimental details

The measurements were made using single-crystal MnO grown by the Verneuil method. In order to remove some higher oxidation states, the crystals were annealed for 3 h at 1273 K in a 10% H_2–90% Ar atmosphere, which yields fully reduced MnO. For the optical measurement, the temperature variation was achieved using an He-gas-flow-type cryostat. An Ar laser (wavelength, 488.0 nm) was used to excite the emission. The emission spectra were obtained using Jobin–Yvon H-20 IR and H-20 UV monochromators with a North Coast Scientific Corporation EO-817L germanium detector or Hamamatsu R316-02 or R928 photomultipliers. The experimental details have already been reported in our previous paper (Mochizuki *et al* 1990). The measurements of photoluminescence were made with the nearly steady-state condition in which the excitation laser beam was mechanically chopped at frequencies of the order of several tens of hertz. The spectral response of the optical system including the focusing lenses and mirrors was carefully measured using a calibrated light source and was used to correct the raw data.

3. Results

Figure 1 shows the photoluminescence spectra of MnO at several temperatures: 5, 35, 55 and 75 K. As shown in this figure, at 5 K, a strong broad emission band (band A) and a weak broad emission band (band B) are observed at 1.76 eV and 1.24 eV, respectively. The Stokes shift of band A is determined to be about 0.25 eV with respect to the lowest crystal-field absorption peak (band E in figure 2 of our previous paper, Mochizuki *et al* (1990)). On increasing the temperature, the emission intensity of band A decreases gradually and the peak energy shifts to a lower energy, while band B increases without a peak-energy shift. At about 30 K, conspicuous drops in the emission intensity and peak energy of band A are observed, while the intensity of band B continues to increase up to about 80 K and then begins to decrease above 85 K. The temperature dependence of the energy E_p at the maximum of band A and the temperature dependences of the peak heights I_p for bands A and B are shown in figures 2 and 3, respectively. The overall emission intensity is lower for samples far from stoichiometry but the spectral shape is not sensitive to this parameter, except for some as-grown crystals which do not show band A emission above 77 K (figure 3 of our previous paper, Mochizuki *et al* (1990)). We also found some shoulders on the higher-energy side of band A; these appear at low temperatures, for instance at 5 K, as shown in figure 4. These side features are similar to those observed in absorption measurements (Yokogawa *et al* 1977). In the absorption study, the fine structures appearing on the lower-energy side of band A were assigned to a side band due to combinations of three kinds of elementary excitation: Mn^{2+} excitons,

magnons and phonons. We assign the four side bands in figure 4 to the following combinations by referring to the above-cited absorption study: side band a to an Mn^{2+} exciton–magnon combination, side band b to an Mn^{2+} exciton–TO-phonon combination, side band c to an Mn^{2+} exciton–magnon–TO-phonon combination and side band d to an Mn^{2+} exciton–LO-phonon combination. In the assignments, we used the frequencies 112 cm^{-1} (Yokogawa *et al* 1977), 270 cm^{-1} (Mochizuki 1989) and 564 cm^{-1} (Mochizuki 1989) as the frequencies of the magnons, TO phonons and LO phonons, respectively. In figure 5, we show the temperature dependence of the side band a, which vanishes above 40 K. The results reported above are independent of the excitation wavelength, apart from the emission intensity. The excitation spectrum at 78 K has already been reported in our previous paper (Mochizuki *et al* 1990). It indicates that the emission occurs via the lowest excited state of Mn^{2+}.
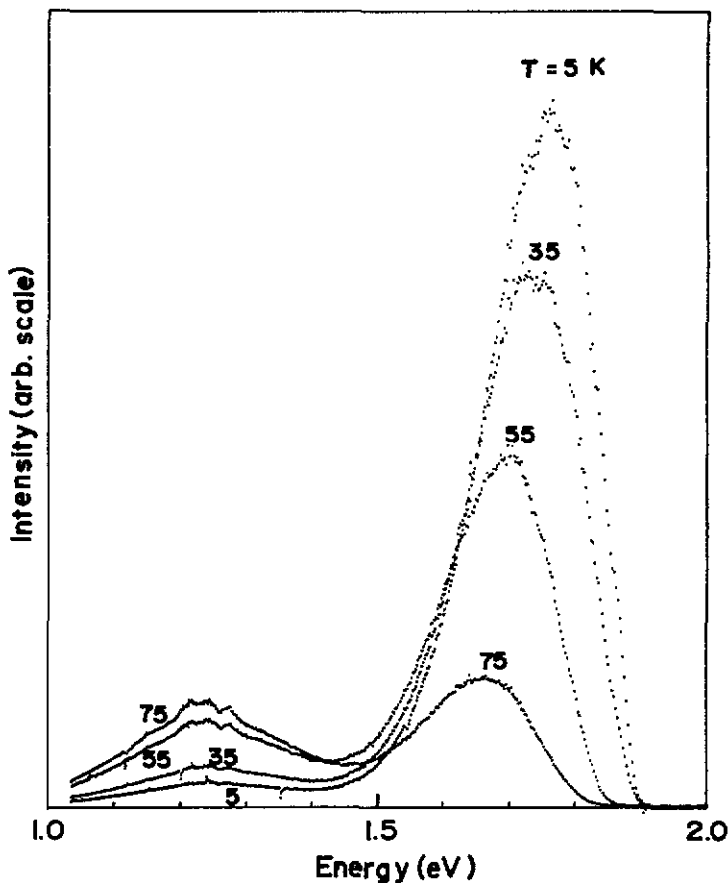

Figure 1. Photoluminescence spectra of heat-treated MnO crystals at various temperatures.

4. Discussion

Both the present results and the previous results (Mochizuki *et al* 1990) on the
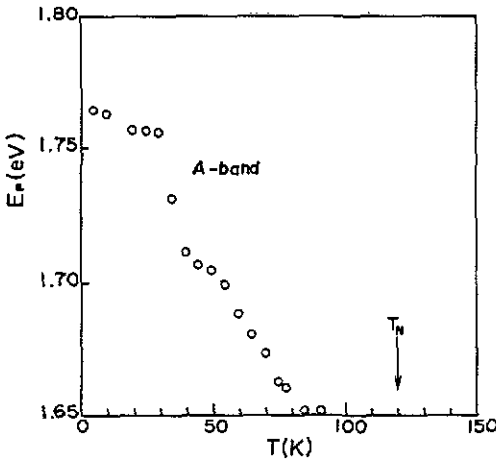
Figure 2. Temperature dependence of the energy at the intensity maximum of band A of heat-treated MnO.
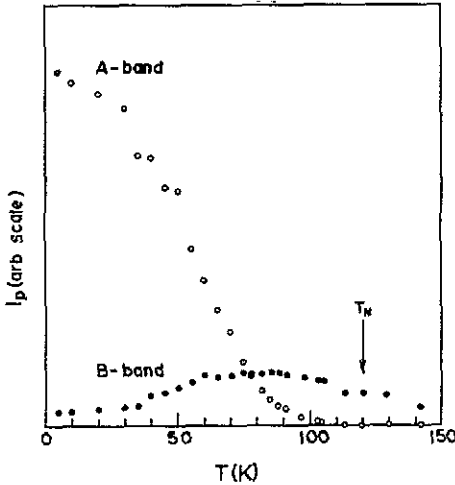

Figure 3. Temperature dependences of the intensities of bands A and B of heat-treated MnO.

photoluminescence of MnO at nearly steady state may be summarized as follows.

(1) The photo-excitations from the sextet ground state of the Mn^{2+} ions to the excited states in MnO induce two broad-band (bands A and B) emissions with large Stokes shifts.

(2) Band A exists only below the Néel temperature, while band B persists and remains in the paramagnetic phase, although a conspicuous drop in the integrated intensity is observed at the Néel temperature, as shown in the previous paper.

(3) On the higher-energy side of band A, sharp side bands due to Mn^{2+} exciton–magnon, Mn^{2+} exciton–TO-phonon, Mn^{2+} exciton–magnon–TO-phonon and Mn^{2+} exciton–LO-phonon combinations are observed.

(4) The observed emission spectra are independent of the excitation photon energy, apart from the intensity.

(5) A conspicuous peak-energy drop of band A occurs at about 30 K $(0.25T_N)$

and, at the same temperature, a discontinuity is observed in the intensity of band B.

(6) Above 30 K, it seems that competition between the intensities of bands A and B occurs.

The results (2) and (3) indicate that the luminescent centres are closely related to the magnetic ordering of Mn^{2+} spins. Moreover, since the observed side band due to the combination of Mn^{2+} excitons and magnons is sharp and single, it is better to consider that band A originates from one kind of Mn^{2+} exciton state. The result (4) indicates that emissions A and B always arise from the same Mn^{2+} lowest excited levels, whatever the upper-lying excited levels are. The result (5) indicates some kind of change in the Mn^{2+} exciton state that could be related to a change in magnetic ordering. The result (6) is coherent with phonon- or thermal-magnon-assisted energy transfer from the luminescence centres of band A to those of band B.
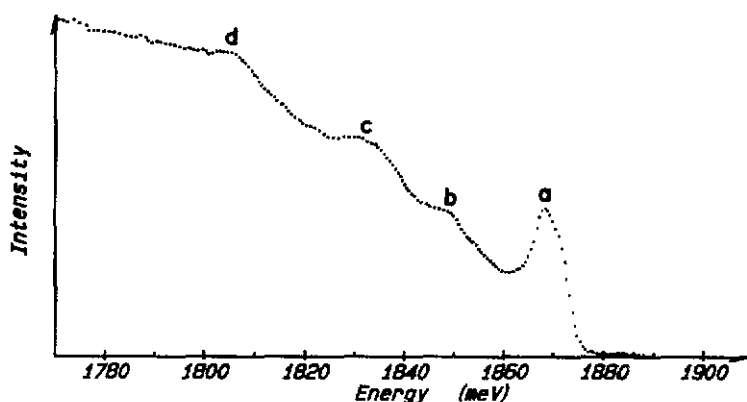

Figure 4. Photoluminescence side-band spectrum of heat-treated MnO at 5 K.

In the previous studies of MnO (Mochizuki *et al* 1990) and MnS (Mochizuki 1990, Mochizuki and Takayama 1991), we have used two models in order to explain the observed large Stokes shift and large width of band A. Model I is based on many different impurity-perturbed Mn^{2+} excitons; model II is based on intrinsic Mn^{2+} self-trapped excitons. In order to interpret the observed results by model I of the spin-wave-assisted photoluminescence due to many different impurity-perturbed Mn^{2+} excitons with various binding energies, we should find many emission lines due to the Mn^{2+}–one-magnon and Mn^{2+}–one-phonon combinations in a broad envelope. However, we found one set of relatively well resolved lines due to such combinations (figure 4). Therefore, we focus our discussion on model II. First, we discuss the large width and the energy position of the band A emission arising from the intrinsic self-trapped Mn^{2+} excitons. In order to conserve energy, momentum and spin, the transition may be accompanied by many types of combination at various orders of the elementary excitations. The convolution of their state densities explains the broad band observed in vibronic spectra of impurity-doped non-magnetic ionic crystals (see, e.g., Nakata *et al* (1991)). In model II, the magneto-elastic interaction depends on the degree of spin alignment and on the ionicity or covalency in the antiferromagnetic bonding. The curvature, the energy value of the potential curve and the lattice distortion on the configurational coordinate diagram shown in the previous paper (Mochizuki and Takayama 1991) depend on both factors. Therefore, the magnitude
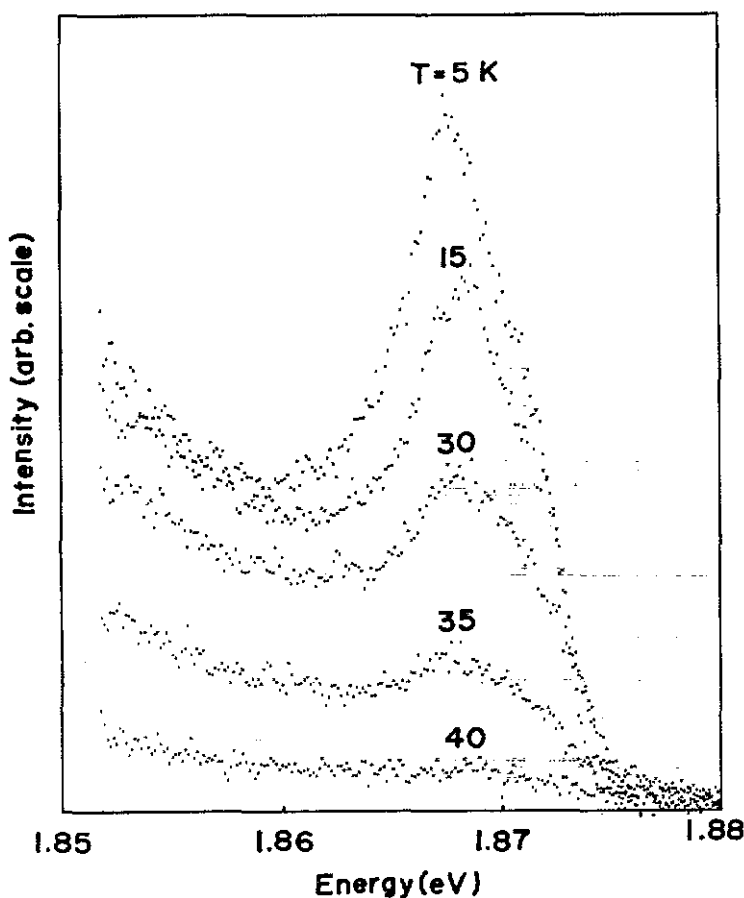
Figure 5. Magnon side-band spectra of heat-treated MnO at various temperatures.

of the temperature shift of the energy at maximum intensity depends on the kind of anion. In fact, in MnO, we have observed a considerable temperature shift in the emission peak energy while, in MnS (Mochizuki and Takayama 1991), such a shift was hardly observed.

Next, we discuss the origin and photoluminescence process of band B. The possible origin for the lower-lying electronic states giving the band B emission may be Mn^{2+} ions perturbed by some crystalline defects, e.g. Mn_3O_4 clusters (Mochizuki *et al* 1990) or impurities (Greene *et al* 1968).

Then, we discuss both the energy transfer from intrinsic self-trapped Mn^{2+} excitons to perturbed Mn^{2+} excitons and the temperature dependence of the band B emission. Whether Mn^{2+} is perturbed or not, the absolute values of spin quantum numbers of the photo-excited state and of the ground state are $\frac{3}{2}$ and $\frac{5}{2}$, respectively. Following the theoretical treatment by Ueda and Tanabe (1980), the motions of excitons which are mostly affected by the temperature are between nearest-neighbour inter-sublattice ion pairs. In this particular case, in order to transfer the excited state from a photo-excited intrinsic Mn^{2+} exciton to a nearest-neighbour perturbed Mn^{2+} ion which is in the ground state, the process must be magnon assisted so that the transfer efficiency increases sharply with increasing temperature. Our experi-
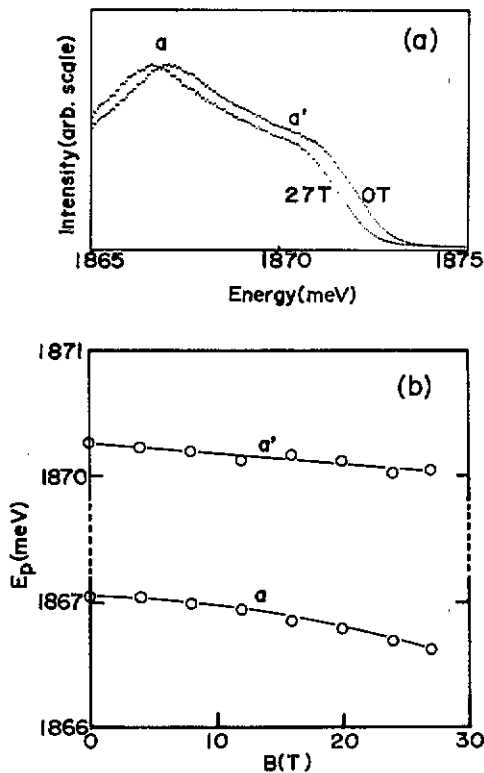
Figure 6. Magnetic field dependence of the magnon side band (band a) and the shoulder band (band a') of heat-treated MnO at 4.2 K.

mental results are consistent with the fact that the magneto-elastic interaction will not perturb significantly the above considerations. Above the Néel temperature, the spin-wave approximation is not useful. However, it has been reported that, above the Néel temperature, the short-range spin order of Mn^{2+} in manganese compounds does persist (Hermsmeier *et al* 1989). If we regard a magnetic lattice with such short-range spin order as a magnetic lattice with spin defects or with a long spatial periodicity, radiative decay assisted by some localized magnetic excitations, in addition to the considerably damped long-wavelength spin-wave excitation, may exist.

Very recently, we have made preliminary measurements on the effect of the magnetic field on the Mn^{2+} exciton–magnon combination band at 4.2 K using a high-resolution monochromatic system. A typical result is shown in figure 6. As seen in figure 6(a), the side band has a shoulder band (band a') on its higher-energy side; band a' shows a different magnetic field dependence from that of the main band (band a). Therefore, in order to discuss in detail and to examine the above-mentioned photoluminescence model II, together with model I, information (pressure and magnetic field effects) on the side-band structure and on the dynamic properties of the photoluminescence is needed. We are now measuring the time-resolved emission spectra of MnO and MnS. Details of the results will be published elsewhere (Mochizuki *et al* 1992).

Acknowledgments

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