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ZERO PHONON LINES OF THE M-CENTER IN ZnS CRYSTALS

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The zero phonon line of the M-center luminescence in ZnS crystals has been detected at 819.76 nm. As a consequence of this the entire structure of the M-band could be explained and a sum rule for zero phonon lines in emission and excitation of deep centers in II-VI semiconductors has been derived.

ZnS crystals exhibit a well known emission band[1] structured by more than 70 narrow lines in the spectral range of 815-900 nm. This luminescence band in ZnS has been attributed to a M-center which is formed by two neighbouring sulfur vacancies (F-centers). The difficulty to explain the entire structure by a combination of phonon replicas arose from the fact that it was, up to now, not possible to determine unambiguously the corresponding zero phonon line. A further experimental peculiarity is that a variety of Ni^{2+} lines with their phonon replicas and wings - even in not intentionally doped ZnS crystals - is superimposed[2] in this energy range. Therefore, it has also been argued that the M-band may be directly connected with a Ni impurity. However, a different excitation behaviour (see fig. 4 in ref. 2) of the Ni^{2+}- and the M-center emissions has been observed. On the basis of these findings we show in the following that indeed a separation of the two luminescence spectra can be achieved. A weak zero phonon line could be discovered which was unknown up to now. All phonon replicas can be shown to belong to this line. Further, an interesting sum rule exists which makes probably an excitation process via deeply bound excitons.

In Fig. 1 we reproduce two emission spectra in the spectral region of 800 nm-860 nm which have been recorded when the crystal was excited with light of different wavelengths (A = 475 nm, B = 590 nm). In spectrum B only the M-center can be excited, whereas in spectrum A both emissions are visible. A clear difference is observable between the two spectra. Several narrow lines which occur in spectrum A are missing in B. In addition, the broad phonon side-band stemming from the Ni^{2+} emission is reduced considerably. Now, the zero phonon line of the M-band appears at λ = 819.76 nm. This is

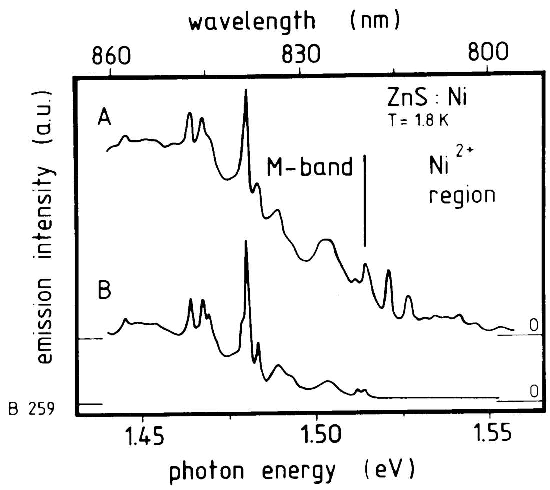

FIGURE 1
Emission spectra of ZnS:Ni. Separation of the M-band from Ni^{2+}-lines by different excitation energies. Curve A shows the superposition of M-luminescence (M-region) and Ni^{2+}-emission (Ni^{2+}-region), E_{exc} = 2,627 eV. The excitation energy of curve B is 2.101 eV.

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shown in Fig. 2. A marks the excitation spectrum of the most intense emission line of B. An overlap in absorption and emission of the zero phonon line is clearly demonstrated. A careful analysis of these spectra leads to a fully understood attribution of all narrow lines to a few phonon energies, in a similar way as has been done in ref. 1. However, in contrast to those results we show that the most intense line is not a zero phonon line but can be deduced from the new zero phonon line taking a TO(Γ) lattice phonon. The short wavelength side of this line is dominated by local phonon replicas with a typical energy distance of 125 cm^{-1}, as has been discussed in ref. 3.

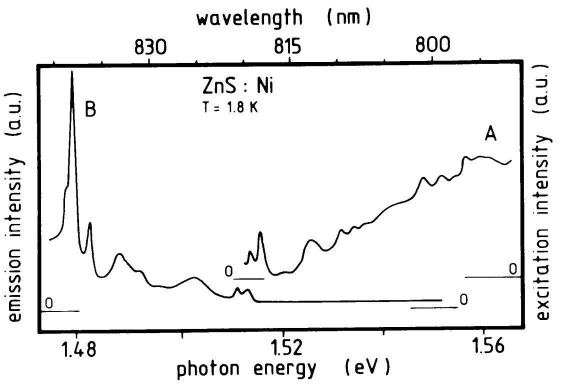

FIGURE 2
Identification of the zero-phonon-line of the M-center. A: excitation spectra of the 1,4787 eV emission-line. B: emission spectra of the M-band E_{exc} = 2,101 eV.

The identification of zero phonon lines in the emission spectrum together with the zero phonon structure already mentioned with respect to the excitation spectra of the M-band (see Fig. 4 in ref. 2) near 534 nm leads to a possible explanation of the excitation mechanism in terms of deeply bound excitons. Comparing the two observed zero phonon energies $h\nu_{emission}$ = 1.5124 eV and $h\nu_{excit}$ = 2.3332 eV we find that the numbers add up to about the energy of the band gap, $h\nu_{excit} + h\nu_{emission}$ = 3.845 eV. A possible explanation of this sum rule is the existence of an excited state of the M-center where a hole as well as an electron are simultaneously bound. Similar sum rules have been detected in different other systems like ZnS-Cu[4], CdS:Cu and ZnS:Ni.

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