Temperature Dependence of the Mn 2+ Concentration in Sintered Mixed Compounds Cd 1-x Zn xS and CdS 1-x Se x

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Temperature Dependence of the Mn^{2+} Concentration in Sintered Mixed Compounds $Cd_{1-x}Zn_xS$ and $CdS_{1-x}Se_x$

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The optical properties of the transition elements, known as deep luminescence centers, in II-VI compounds have been discussed so far by the crystalline field theory, and the various crystal field states of the ions have been identified.[1] However, much less is known about the location of these localized states with respect to the energy bands of the host crystal, and now it is of current interest for the understanding of the excitation process or energy transfer. Recently Langer, *et al.* have made it clear from the kinetic energy distribution of electrons emitted from samples due to X-ray excitation that the Mn-level in ZnS lies about 3 eV below the top of the valence band.[2] As an another approach to the problem, we have employed the EPR technique to get information about the temperature dependence of the Mn^{2+} concentration in $Cd_{1-x}Mg_xTe$ $(0<x<0.25)$ mixed single crystals and discussed on the charge transfer mechanism associated with the Mn^{2+}-levels in the energy band.[3]

In this paper are reported the similar experimental results carried out on Mn (0.02%)-doped mixed compouds $Cd_{1-x}Zn_xS$ and $CdS_{1-x}Se_x$. The samples used were sintered powders, simply because the preparation method is easy and the hyperfine structures are independent on the crystal direction. The measuring apparatus and analysis were the same as the previous work.[3] The sample preparation and other EPR studies for the present two mixed compounds will be described in another paper.

The area under the observed absorption curves S of the $(M=\frac{1}{2},\ m=-5/2)$ hyperfine line of the Mn^{2+}-doped samples were measured as a function of temperature. As in the previous study, the signal intensity S may be expressed at high temperature approximation as $S \propto N/T$, where N is the total number of the Mn^{2+} ions responsible for the EPR spectrum observed. The experimental values of ST $(\propto N)$ are shown in Fig. 1 against the reciprocal temperature for $Cd_{1-x}Zn_xS$. The similar curves were also obtained for $CdS_{1-x}Se_x$. The values can be fitted to a form with two activation energies ε_1 and ε_2 as

$$ST \propto N = c_1 \exp(\varepsilon_1/kT) + c_2 \exp(\varepsilon_2/kT), \cdots\cdots\cdots(1)$$

where c_1 and c_2 are the constants. From the slopes at the low temperature side the energy ε_2 can be obtained and it is plotted against the composition x in Fig. 2, while ε_1 at the high temperature side is not definitely determined for the two systems. ε_1 was found almost composition-independent for $Cd_{1-x}Mg_xTe$, being 0.08 eV.[3] In Fig. 2

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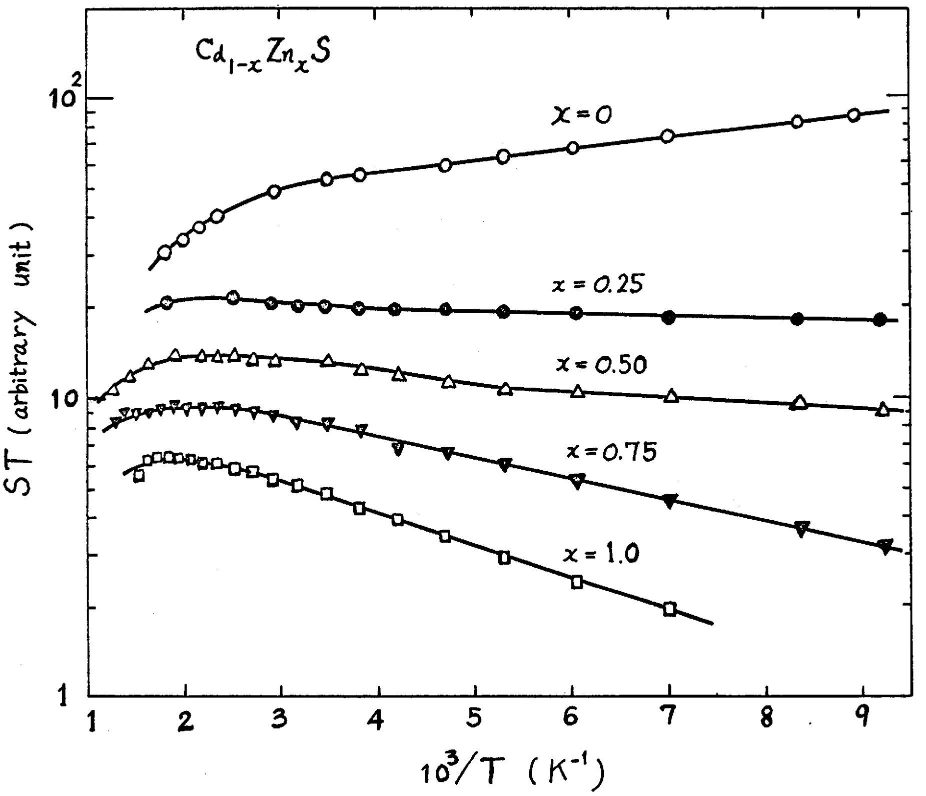

Fig.1. The temperature dependence of the Mn^{2+} concentration for $Cd_{1-x}Zn_xS$ against the reciprocal temperature in arbitrary unit.

are also shown the values of $Cd_{1-x}Mg_xTe$ for comparison. It is noted that ε_2 of ZnS (band gap E_g=3.6 eV) is large and negative, in contrast with those of CdS (E_g = 2.41 eV), CdSe (E_g = 1.67 eV), and MgTe (E_g = 4.7 eV).

Although the Mn^{2+}-states in the energy band cannot be identified from the present studies, it may be pointed out that the activation energies ε_2 increase with the band gap. This is not, however, the case for $Cd_{1-x}Zn_xS$ system. The charge transfer mechanism for the Mn^{2+}-states may also be applied to the present case as in the previous work.[3] This work will also be submitted to J. Phys. Soc. Japan. We thank Prof. H. Yagi for his encouragement throughout this study.

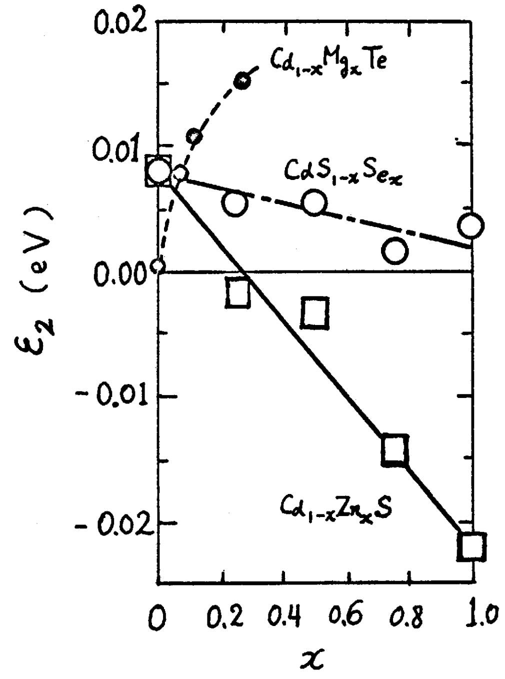

Fig. 2. The activation energy ε_2 against x for $Cd_{1-x}Zn_xS$ shown by (□), for $CdS_{1-x}Se_x$ by (○), and for $Cd_{1-x}Mg_xTe$ by (●).

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Note added in proof

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