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Effect of the Second Coordination Sphere on the Electron Transition Energies in ZnS – Mn

Short Communication

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The influence of the second coordination sphere on the energy of electron transitions in ZnS – Mn is investigated using the crystal field theory. The obtained perturbation effect is small and may be usually neglected.

(Keywords: Electron transition energies in ZnS – Mn; *Manganese activated zinc sulphide; Effect of the second coordination sphere)*

Einfluß der zweiten Koordinationssphäre auf die Energie der Elektronenübergänge in ZnS – *Mn (Kurze Mitteilung)*

Der Einfluß der zweiten Koordinationssphäre auf die Energie der Elektronenübergänge in ZnS – Mn wird mit Hilfe der Kristallfeldtheorie untersucht. Es ergibt sich, daß der Störeffekt klein ist und gewöhnlich vernachlässigt werden kann.

The electron transitions in manganese activated zinc sulphide have been considered so far on the basis of crystal field theory by taking into account the effect of the first coordination sphere on the activator ion[1–5]. In this communication the influence of the potential generated by the second coordination sphere in cubic ZnS – Mn is assessed.

The symmetry of a cluster consisting of a manganese ion, incorporated in the crystal, and the surrounding ions should be invariant with respect to the number of the coordination spheres because all odd number spheres have T_d symmetry, and the even number spheres have O_h symmetry. Having in view that the ions which form the coordination spheres of T_d symmetry have negative charges whereas the spheres of O_h symmetry consist of positive ions it may be expected that the direction of the shift of the split *d*-AO would be the same for a cluster containing the ions from both the first and the second coordination spheres as for a cluster in which only the ions from the first sphere participate. The energy of the splitted *d*-orbitals, however, should be changed under the action of the second coordination sphere. This energy change is calculated perturbationally applying the crystal field theory.

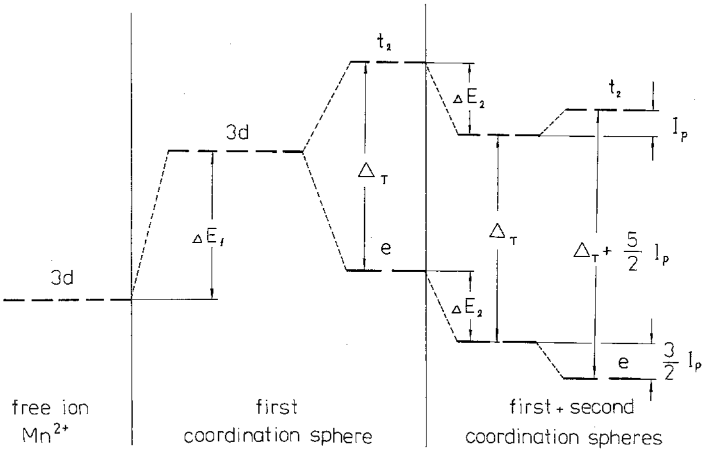

Fig. 1. Splitting of the *d*-orbitals of Mn(II)

It is known that the potential of an octahedral crystal field is:

$$V_{O_h}(r, \theta, \varphi) = A_{00} r^0 Y_{00} + A_{40} r^4 [Y_{40} + \sqrt{5/14}(Y_{4-4} + Y_{44})]$$

where the ligand coefficients A_{00} and A_{40} are given in the form of spherical harmonics:

$$A_{\mu\nu} = -\frac{4\pi}{2\mu + 1} \cdot \frac{q}{R^{\mu+1}} \sum_k Y^*_{\mu\nu}(\theta_k, \varphi_k) = a_\mu \sum_k Y^*_{\mu\nu}(\theta_k, \varphi_k)$$

Taking into account the real values for the twelve zinc ions in the second coordination sphere, one obtains for the potential energy:

$$H_p = -\frac{12qe}{R} + \frac{7\sqrt{\pi}\, q r^4}{6R^5}\left[\frac{3}{16\sqrt{\pi}}(35\cos^4\theta - 30\cos^2\theta + 3) + \right.$$

$$\left. + \frac{5}{16}\sqrt{\frac{61}{7}} \sin^4\theta (\sin 4\varphi + \cos 4\varphi)\right]$$

The first term in the expression for H_p has the same value for both the t_2- and e-orbitals, and because of this an equal displacement ΔE of their energy levels occurs. Therefore the calculation of the potentional energy matrix is made using only the second term in the expression given above. In this way a decrease in the t_2- and e-orbital energy is obtained equal to $\Delta E - I_p$ and $\Delta E + \frac{3}{2} I_p$, respectively when the second coordination sphere is taken in consideration as well (Fig. 1).

As far as it is not possible to estimate the parameter λ arising in the power expansion of the energy for the perturbation, we have taken the λ value equal to 1 which corresponds to the case of the maximal influence of the potential due to the second coordination sphere. Thus the total increase of the splitting parameter Δ_T is calculated to amount at most to $15\,\mathrm{cm}^{-1}$ ($I_p = 6\,\mathrm{cm}^{-1}$) which means the shift in the absorption band to shorter waves cannot exceed 0.1 nm. This result shows that in most cases the influence of the second coordination sphere may be neglected.

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References

[1] *Bethe H.,* Ann. Physik **5**, 3, 135 (1929).

[2] *McClure D. S.,* J. Chem. Phys. **39**, 2850 (1963).

[3] *Ford R. A., Kauer E., Rabenau A., Broson D. A.,* Ber. Bunsenges. Phys. Chem. **67**, 460 (1963).

[4] *Curie D.,* C. r. Acad. Sci. **258**, 3269 (1964).

[5] *Gumlich H. E., Pfrogner R. L., Schäffer I. C., Williams F. E.,* J. Chem. Phys. **44**, 10, 3239 (1966).