acta phys. slov. 23 (1973), No. 1

ZERO-FIELD SPLITTING OF THE S-STATE OF THE Mn^{2+} ION ON $MgSO_4 \times 7H_2O$

ONDREJ BARTKO*, Košice

Several mechanisms were suggested to explain the splitting of the S-state of paramagnetic ions in the electric field of a crystal. Sharma, Das, Orbach [1], [2], [3], [4] performed quantitative theoretical calculations of the spin-Hamiltonian parameters D, E of Mn^{2+} in ZnF_2 and in MnF_2 and of $Fe_3{}^+$ in MgO. They showed that in these cases the most important contribution came from the Blume-Orbach (BO) mechanism [5] involving the first-order matrix elements of the axial and rhombic fields between excited quartet states admixed by the cubic component of the crystalline field. The contribution of the other mechanisms, the spin-spin mechanism (Pryce [6]), the Watanabe mechanism (WC) and the Orbach-Das-Sharma mechanism (ODS) were essentially smaller than those from BO. Wybourne [7] and Van Heuvelen [8] considered the relativistic effects on the splitting of the S-state ions. They used the relativistic Hartree-Fock wavefunctions in the crystal field calculations.

The aim of this paper is to determine theoretically on the basis of the mentioned mechanisms the parameters of the spin-Hamiltonian, to show the importance of the here considered mechanisms and to compare the computed values with the experimental values for the Mn^{2+} ion in the crystal field of $MgSO_4 \times 7H_2O$.

The contributions of the considered mechanisms to D and E are:

a. the BO mechanism

$$D_{BO}\ \frac{\langle {}^6S|H_{SO}|{}^4\Gamma_4\rangle\langle {}^4\Gamma_4|\mathscr{H}_{ax}|{}^4\Gamma_4\rangle\langle {}^4\Gamma_4|\mathscr{H}_{SO}|{}^6S\rangle}{[E({}^4\Gamma_4)-E({}^6S)]^2}. \tag{1}$$

In the calculations, the spin-orbit coupling parameter ξ has been put equal to 300 cm^{-1} [1], the cubic field splitting parameter equal to 10 Dq = 9000 cm^{-1} [9] and $\langle r^4\rangle = 5.5126\, a_0^4$ (a_0 — radius of the first Bohr's orbit) [3]. The obtained value of contribution to D is

$$D_{BO} = 8.86\, B_4^0, \tag{2}$$

and for the parameter E

$$E_{BO} = -\,11.03\, B_4^2. \tag{3}$$

The crystalline field components B_l^m are in units of $e^2/2a_0^5$.

* Katedra fyziky VŠT, KOŠICE, Komenského park 2.

b. The relativistic mechanism

$$D_r \sim \frac{2\langle {}^6S|\mathscr{H}_{SO}|{}^4P\rangle\langle {}^4P|B_2^0 b_2(11)W^{(11)2}|{}^6S\rangle}{E({}^4P)-E({}^6S)}, \tag{4}$$

where $W^{(11)2}$ is the single-particle double-tensor operator defined by Judd [10], $b_2(11)$ the radial integral [7]. The values of contributions to the constants D and E are:

$$D_r = \frac{6}{125} B_2^0 \frac{\xi}{E_P}\left(-\,4R_{++}^2 + R_{--}^2 + 3R_{+-}^2\right), \tag{5}$$

$$E_r = \frac{2\sqrt{6}}{125} B_2^2 \frac{\xi}{E_P}\left(-\,4R_{++}^2 + R_{--}^2 + 3R_{+-}^2\right), \tag{6}$$

where ξ is the spin-orbit coupling parameter, $R_{jj'}^k$ are the radial integrals from the relativistic radial functions (+ — for all possibilities $j = l \pm \frac{1}{2}$; $j' = l \pm \frac{1}{2}$), $E_P = E({}^4P) - E({}^6S)$. The values of the integrals $R_{jj'}^k$ have been calculated for various ions by Waber and Cromer [11]. For the Mn^{2+} ion they are equal to

$$(-4R_{++}^2 + R_{--}^2 + 3R_{+-}^2) = -\,0.0485\, a_0^2. \tag{7}$$

Substituting (7) and the values $\xi = 300\ cm^{-1}$, $E_P = 30000\ cm^{-1}$ into (5) and (6) we have

$$D_r = -\,2.55\, B_2^0, \tag{8}$$

$$E_r = -\,2.08\, B_2^2;$$

B_l^m are in units of $e^2/2a_0^3$.

For the calculation of the contributions of the spin-spin mechanism we use the results [1]:

$$D_{ss} = -\,0.21915\, B_2^0, \tag{9}$$

$$E_{ss} = -\,0.09269\, B_2^2.$$

Using the point-charge model, the crystalline field components B_l^m were computed by the direct method of the lattice summation [4], assuming two units of a negative charge on the O^{2-} sites and from the SO_4 groupe. Values of ion positions given by Baur [12] were used. A computer program was used to carry out the calculation over a sphere with the radius of $r = 1.5\, c$ with the centre on the central Mn^{2+} ion site; $c = 6.857$ Å is the lattice constant. The choice of the coordinate system is in agreement with the axes of the crystal field determined by the EPR expreriment [13]. The calculated values of the crystalline field components are:

$$B_2^0 = -\,114.62 \times 10^{-4} \qquad B_4^0 = +\,20.36 \times 10^{-4} \tag{10}$$

$$B_2^2 = +\,1.29 \times 10^{-4} \qquad B_4^2 = -\,2.25 \times 10^{-4}.$$

In Table 1 there are given the resulting calculated values of the constants D, E, the contributions of the considered mechanisms and the values obtained from the EPR experiment [13].

From the comparison of the contributions of the individual mechanisms it appears that the dominant cintribution to the constant D comes from the relativistic mechanism, while for the rhombic constant E from the BO mechanism. The resulting contributions

Table 1

mechanism	$D \times 10^4$ [cm^{-1}]	$E \times 10^4$ [cm^{-1}]
spin-spin	25.1	− 0.12
BO	176.5	+24.81
relativistic	292.3	− 2.68
total	492.3	22.0
experiment	399.8	13.5

of the WC and ODS mechnisms are negligible in comparison with the smallest contribution of the spin-spin mechanism and for that reason not included in the calculations.

The comparison of the calculated values with the experimental results shows that the splitting of the S-state Mn^{2+} ion in the crystal field of $MgSO_4 \times 7H_2O$ can be reasonably accurately characterized with the help of the three here considered mechanisms.

The value of the hyperfine constant from the EPR experiment [13] $A = 90 \times 10^{-4}$ cm^{-1} is smaller than that for Mn^{2+} in a pure ionic crystal $A = 100 \times 10^{-4}$ cm^{-1} [14]. This is consistent with the well-known fact that covalent bonding in crystals reduces the value of A. We asume from this fact that the eventual including of covalent effects not included in the calculation, would improve the agreement with the experiment. It would, however, mean that the contributions to constants D, E from the covalent effects will be in our case negative.

I am indebted to Prof. M. Rákoš for stimulating helpful discussions and suggestions.

REFERENCES

[1] Sharma R. R., Das T. P., Orbach R., Phys. Rev. *149* (1966), 257.
[2] Sharma R. R., Das T. P., Orbach R., Phys. Rev. *155* (1967), 338.
[3] Sharma R. R., Das T. P., Orbach R., Phys. Rev. *171* (1968), 388.
[4] Sharma R. R., Phys. Rev. *176* (1968), 467.
[5] Blume M., Orbach R., Phys. Rev. *127* (1962), 1587.
[6] Pryce M. H. L., Phys. Rev. *80* (1950), 1107.
[7] Wybourne B. G., J. Chem. Phys. *43* (1965), 4506.
[8] Van Heuvelen A., J. Chem. Phys. *46* (1967), 4903.
[9] Jorgensen C. K., *Absorption Spectra and Chemical Bonding in Complexes*. Pergamon Press, New York 1962.
[10] Judd B. R., *Operator Techniques in Atomic Spectroscopy*. McGraw-Hill, New York 1963.
[11] Ja Y. H., Australian J. Phys. *23* (1970), 299.
[12] Baur W. H., Acta Cryst. *17* (1964), 1361.
[13] Bartko O., Disertation, 1971.
[14] Title R. S., Phys. Rev. *131* (1963), 263.

Received May 22d, 1972.