

Letters to the Editor

THE INFLUENCE OF COVALENCY ON THE ZERO-FIELD SPLITTING OF THE S-STATE OF THE Mn^{2+} ION IN TiO_2

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Recently, Sharma, Das, Orbach [1, 2, 3], have suggested two models in order to explain the zero-field splitting of the S -state of the paramagnetic Mn^{2+} ion located in the crystal electric field. The first of them, the point multipole model involves the electrostatic deformation of the electronic cloud of the paramagnetic ion due to the potential produced by the charge distribution of the neighbouring atoms. In the second, the "Overlap and Covalency Model", there was considered the overlap of electron orbitals of the paramagnetic ion with those of electrons of ligands taking part in covalent bonds. These two models were applied to the cases of Mn^{2+} ion in ZnF_2 and in MnF_2 [1, 2] and the Mn^{2+} ion in MgO [3]. The results of these papers have shown that the contributions to the constants of the spin Hamiltonian arising from the use of the second model are negligible.

The purpose of this paper is to investigate the influence of covalency on the splitting of the S -state of the Mn^{2+} ion in the TiO_2 crystal (rutile) using the suggested model in [2, 3] and also to verify the applicability of the model for the case in which the covalent binding between the central ion and the ligands is dominant.

Since the zero-field splitting of the S -state of the paramagnetic ion is characterized with the help of the constants D , E in the spin Hamiltonian

$$H_s = D[3S_z^2 - S(S+1)] + E(S_x^2 - S_y^2), \quad (1)$$

the investigation of the problem consists in the determination of the parameters D , E . The Mn^{2+} ion in TiO_2 is found in the centre of the octahedron on the Ty^+ site. According to [4], four ions of oxygen (O_{eq}) have the same distance from the central ion $a_1 = 1.944$ Å, while for the two remaining ones (O_{ax}) the distance is $a_2 = 1.988$ Å. The angle between the lines joining the two neighbouring ions O_{eq} with the central ion is different from $\pi/2$ ($\cos \beta = -0.1593$). The point-group symmetry at the Mn^{2+} site is orthorhombic.

The calculation of the constants of the spin Hamiltonian D , E was realized analogously to the procedure outline in [2], [3] involving the appropriate peculiarities. In the calculation we have considered the overlap of the $3d$ electron orbitals of the Mn^{2+} ion with all $2s$, $2p_x$, $2p_y$, $2p_z$ electron orbitals of the O^{2-} ions. The constants D , E were expressed with the help of the overlap integrals and double two-center integrals involving spin-spin and spin-orbit interactions. These integrals have been determined with the help of

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Löwdin's α -function method [5]. The desirable α -functions have been derived from the general analytical expressions in [6] after the necessary corrections. The functions α are the radial parts in the expansion of the wave functions for oxygen with Mn^{2+} ion as the centre. Explicitly, they are defined as

$$\psi(O|LM|R, \Theta, \Phi) = \sum_{l=0}^{\infty} r^{-l} \alpha_l(O|LM|\alpha r) Y_l^M(\theta, \phi), \quad (2)$$

where (R, Θ, Φ) are the polar coordinates of a point with respect to the oxygen ion, the polar axis being taken as the line joining Mn^{2+} and the O^{2-} ion under consideration; (r, θ, ϕ) represent the polar coordinates with the same polar axis but with Mn^{2+} as the origin. The quantities L, M characterize the electron orbitals of the oxygen ion: $2s(L=0, M=0)$, $2p(L=1, M=1)$, and $2p(L=1, M=\pm 1)$; α being the distance between the central and the ligand ions.

For the determination of the α -functions and for the calculation of the overlap and the two-centre integrals we have used the analytical expressions according to [7] as the radial part of the wave function of the $3d$ electrons of the Mn^{2+} ion. As regards to choice of the radial part of the wave function for the O^{2-} employed for the calculation, we use the $2p$ and the $2s$ wave functions as used by [8] and [9], respectively. The calculation of the contributions arising from the spin-orbit interaction has been performed with the help of the known values of the constant of the spin-orbit coupling: $\xi_{d,d} = 300 \text{ cm}^{-1}$ for the Mn^{+2} and $\xi_{p,p} = 67 \text{ cm}^{-1}$ for the O^{2-} ion. The distance of the excited $4P$ state for the ground state 6S is $\Delta = 29.3 \times 10^3 \text{ cm}^{-1}$.

Table 1a

D in units of 10^{-4} cm^{-1}

Mechanism	local	nonlocal	distant	total
Spin-spin	361.5175	-712.5870	0	-361.0695
Spin-orbit	583.9517	6.7160	852.4478	1444.1455
Total				1083.0460
Experimental				1359.79

Table 1b

E in units of 10^{-4} cm^{-1}

Mechanism	nonlocal	distant	total
Spin-spin	1500.4727		1500.4727
Spin-orbit	46.3630	-712.0645	-665.7015
Total			834.7712
Experimental			1306.87

The computation of the constants D, E was performed with the computer Minsk 2/22. The results, the values of the individual contributions, the total theoretical values and the experimental values determined by the EPH method [10] are listed in the Tables 1a and 1b for D and E , respectively.

In the absence of any knowledge of the charge-transfer coefficients, we are unable to include its effect and calculate the contributions to D, E which arise from the overlap alone.

The individual contributions to the constants D, E , listed in the Tables 1a, 1b represent the contributions from the considered spin-spin and spin-orbit interactions: in the region of the central ion — "local", in the region of the ligands — "distant" and "nonlocal" in the region between the central ion and the ligands.

In calculating the individual contributions to D, E we have found that the contributions arising from the effects of the overlap of the $2s$ orbitals of the electrons of the oxygen ion are about two orders smaller than those from the $2p\sigma$ and the $2p\pi$ orbitals. From the comparison of the individual contributions to D it follows that in the investigated case the spin-orbit interaction plays a dominant part. The total contribution arising from the spin-spin interaction is negative and it reduces the resulting effect. The sign of the resulting calculated value of D is positive, this is connected with the fact that the distance of the ligands O_{ax} from the central ion are greater than those of O_{eq} . For the constant E the spin-spin interaction is dominant.

If we compare the resulting calculated values with the experimental ones we find that the calculated values D and E are equal to $\sim 80\%$ and $\sim 64\%$ of the experimental data, respectively. With respect to the negligence of the charge-transfer effect the used model describes the splitting of the S -state of the investigated ion reasonably well.

One can conclude from the results obtained in this paper that the overlaps of the $2p\sigma$ and the $2p\pi$ orbitals of the electrons of oxygen ions with the orbitals of the electrons of the central ion essentially influence the splitting of the S -state of the Mn^{2+} ion in TlO_2 . The character of the bond of the central ion with the ligands is thus the determining factor for the magnitude of the splitting of the S -state of the Mn^{2+} ion.

The author is indebted to Prof. M. Rákoš for helpful discussions and to G. Andrejková for valuable help in programming the computations.

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Received April 8th, 1974