GROUND-STATE SPLITTING FOR d^5 ^6S IONS IN A CUBIC FIELD

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The calculations of Watanabe[1] have been used to interpret paramagnetic resonance experiments on d^5 ^6S ions by Walsh[2] and others.[3-5] Watanabe omitted the spin-doublet states of the configuration d^5, and treated the crystal field, spin-orbit, and spin-spin interactions as perturbations of the free-ion Hamiltonian.

By using a Ferranti Mercury computer and making full use of group theory, we have been able to perform a more refined calculation. Our results differ very considerably from those of the Watanabe theory.

Our calculation includes the spin-doublet states of d^5, treats the crystal field as part of the unperturbed Hamiltonian, and the spin-orbit W_{SO} and spin-spin W_{SS} interactions as perturbations. The perturbation calculation was taken to sixth order. We calculate the following four cases.

(1) Splitting by $(W_{SO}+W_{SS})$ taking account of the spin doublets.

(2) As in (1) but omitting the doublet states.

(3) As in (1) but omitting W_{SS}.

(4) As in (1) but omitting doublets and W_{SS}.

As an example, taking $B=0.9\times10^3$ cm^{-1}, $C=3.3\times10^3$ cm^{-1} for the Racah[6] parameters, $\lambda=0.4\times10^3$ cm^{-1} for the spin-orbit parameter, and $M_0=0.2042$ cm^{-1} and $M_2=0.0159$ cm^{-1} for the spin-spin parameters (calculated from Watson's[7] wave functions for Mn^{++}), and a range of values for the cubic field parameter Dq, we compute the values of the ground-state splitting $3a=E(\Gamma_8)-E(\Gamma_7)$ given in Table I.

There are several points of interest in these results:

(a) Omitting the spin-doublets of d^5, as Watanabe did, reduces the calculated splitting by almost two orders of magnitude.

(b) From a consideration of the variation of the splitting with Dq for practical values of Dq, it is clear that the effect of the cubic field cannot be approximated by second order terms with fourth order corrections, as has been suggested.[1]

(c) The splitting is not an even function of Dq. Watanabe's argument that only even terms occur fails because on going from a description in terms of electrons to one in terms of holes, the signs of both λ and Dq must be reversed. Therefore functions which are odd in both parameters cannot be excluded. However, we agree with Watanabe that the original suggestion of Van Vleck and Penney[8] must be incorrect because it is odd in Dq and even in λ.

(d) For practical Dq values, the contribution from spin-spin interaction is negligible compared to that from spin-orbit interaction. However, in the approximation of neglecting doublets we agree

Table I. Calculated ground-state splitting in Mn^{++}, in units of 10^{-4} cm^{-1}, for given parameters.

Dq cm^{-1}	With spin-spin		Without spin-spin	
	With doublets	Without doublets	With doublets	Without doublets
+1200	89.7	0.971	80.2	-2.08
+1000	46.8	0.784	42.1	-1.08
+ 800	23.1	0.513	21.1	-0.547
+ 600	9.81	0.264	9.45	-0.260
+ 400	2.65	0.0824	3.06	-0.107
+ 200	-0.335	-0.00903	0.178	-0.0301
0	0	0	0	0
- 200	3.56	0.115	2.40	-0.00825
- 400	11.0	0.338	7.86	-0.0622
- 600	23.8	0.668	17.7	-0.188
- 800	45.1	1.09	34.4	-0.443
-1000	81.4	1.59	63.6	-0.937
-1200	146	2.07	117	-1.89

with Watanabe that spin-spin is more important than spin-orbit, although we do not agree quantitatively with his calculations because he has used the large value of $M_0 = 0.642$ and also appears to have used an incorrect perturbation formula.

The main uncertainty in a comparison with experiment is due to the uncertainty in the values of the parameters B, C, λ, and Dq, the calculated splitting being particularly sensitive to C, λ, and Dq. Because of this it is very desirable that optical and electron paramagnetic-resonance experiments should be done on the same material. This uncertainty affects the value of Dq which we calculate from a given a. However, Low has reported the following ground-state splittings: $3a = 56\times10^{-4}$ cm^{-1} for Mn^{++} in MgO, $3a = 24\times10^{-4}$ cm^{-1} for Mn^{++} in ZnS, and $3a = 615\times10^{-4}$ cm^{-1} for Fe^{+++} in MgO.

Assuming the B, C, and λ values used to calculate Table I, we find $Dq = +1050$ cm^{-1} for Mn^{++} in MgO and $Dq = -600$ cm^{-1} for Mn^{++} in ZnS; and for Fe^{+++} (taking free ion values $B = 1.1\times10^3$ cm^{-1}, $C = 4.0\times10^3$ cm^{-1}, together with Kotani's[9] value $\lambda = 0.44\times10^3$ cm^{-1}, and $M_0 = 0.2902$ cm^{-1}, $M_2 = 0.0228$ cm^{-1} from Watson's wave functions) we calculate $Dq = 2150$ cm^{-1}. The predicted Dq value for Mn^{++} in MgO agrees with Pratt and Coelho's[10] value of $Dq = 979$ cm^{-1} in MnO which has the same structure and almost the same lattice constant. (Pratt and Coelho give values of B, C, and Dq which lead to $3a = 60\times10^{-4}$ cm^{-1}.) The values for Mn^{++} in ZnS and Fe^{+++} in MgO agree roughly with the conclusions of Orgel,[11] and the ratio of Dq values for Mn^{++} and Fe^{+++} in MgO is the same as that found by Holmes and McClure[12] in hydrated salts. When optical and electron paramagnetic resonance data on the same material become available, it will be possible to apply the more stringent test of comparing calculated and experimental values of the splitting.

In comparing with Walsh's experimental values of $(\partial\ln a/\partial\ln V)_T$, large uncertainties arise because we have no proper theory to predict $\partial\ln Dq/\partial\ln V$, $\partial\ln\lambda/\partial\ln V$, etc. The simple ionic model gives $\partial\ln Dq/\partial\ln V = -5/3$, but since the model is probably not reliable and we have no values of $\partial\ln\lambda/\partial\ln V$, etc., we can only calculate values of $\partial\ln Dq/\partial\ln V$ from the experimental results and our theory, assuming that λ, B and C remain constant under dilatation.

With this assumption our deductions from Walsh's results are $\partial\ln Dq/\partial\ln V = -2.1$ for Mn^{++} in MgO, $\partial\ln Dq/\partial\ln V = -1.6$ for Mn^{++} in ZnS, and $\partial\ln Dq/\partial\ln V = -0.9$ for Fe^{+++} in MgO.

To conclude, the values of Dq which we deduce are in as good agreement with experiment as can be expected in view of the uncertainties in the model, but using our theory and the experimental results of $\partial\ln a/\partial\ln V$ we deduce various values of $\partial\ln Dq/\partial\ln V$ which are quite different from the values of $-5/3$ predicted by an ionic model.

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