Ground-state zero-field splitting for the Fe^{3+} ion in a cubic field

Kuang Xiao-Yu and Chen Zhong-Hou
Department of Chemistry, Sichuan Normal University, Chengdu 610066, China
(Received 31 October 1986)

At present the parameter a of the Fe^{3+} ion in a crystal has still not been determined. In this paper we discuss this problem by diagonalizing the complete matrices for a ligand-field spin-orbit-coupling perturbation. The results obtained are in good agreement with experimental findings. Furthermore, possible resonances for the difference between our results and previous ones are given.

I. INTRODUCTION

The ground-state zero-field splitting for the Fe^{3+} ion in a cubic field has been extensively investigated by many workers,[1-4] and great progress has been made, but their results cannot be used to determine the parameter a for the Fe^{3+} ion in a crystal. In this paper, a calculation has been performed for the Fe^{3+} ion in $Fe(H_2O)_6^{3+}$, beryl, and MgO crystals by using the crystal-field spin-orbit-coupling mechanism. Our results are considerably different from those obtained in previous work.

II. EPR SPECTRA AND *d-d* TRANSITION ENERGY OF THE Fe^{3+} ION IN VARIOUS CRYSTALS

By taking the same values of the electrostatic parameters, the spin-orbit-coupling coefficient, and the Tress correction as those of Low and Rosengarten[3] ($B=730$ cm^{-1}, $C=3150$ cm^{-1}, $\zeta=420$ cm^{-1}, and $\alpha=90$ cm^{-1}), we obtain the *d-d* transition energy and the parameter a for the Fe^{3+} ion in various crystals, as listed in Table I. The crystal-field parameter Dq is taken from Low and Rosengarten[3] for $Fe(H_2O)_6^{3+}$ and $MgO:Fe^{3+}$ and from Holmes and McClure[5] for beryl. As shown in Table I, the *d-d* transition energy and the parameter a can be interpreted by the crystal-field spin-orbit-coupling mechanism.

III. THE COMPARISON OF OUR RESULTS WITH THOSE OF LOW AND ROSENGARTEN

The cubic zero-field splitting for the Fe^{3+} ion in crystals has been investigated by Low and Rosengarten[3] (LR). They assumed that the admixture of the Γ_8 levels and Γ_6 and Γ_7 levels coming from the same Γ_L is not very different;[3] so, their calculation cannot be used to interpret the EPR spectra and *d-d* transition energy for the Fe^{3+} ion in crystals. The comparison of our results with those of LR is listed in Table II. As remarked by LR, their calculated values for the Fe^{3+} ion are found to be too small by a factor of 2 to 4 when the free-ion spin-orbit-coupling coefficient is used. However, from Table II we see that our data for the ground-state splitting are greater by a factor 2–4 than those of LR, which implies that a reasonable result for the Fe^{3+} ion in a crystal can be obtained by using the crystal-field spin-orbit-coupling mechanism and that the assumption used in LR's calculation is not valid for the Fe^{3+} ion.

IV. THE COMPARISON OF OUR RESULTS WITH THOSE OF POWELL, GABRIEL, AND JOHNSTON

Another interesting result is obtained when we calculate the cubic zero-field splitting $3a$ by using the parameters B, C, ζ, and Dq given by Powell, Gabriel, and

TABLE I. *d-d* transition energy and zero-field splitting (ZFS) $3a$, all numbers in units of cm^{-1}.

(a) *d-d* transition energy						
$Fe(H_2O)_6^{3+}$ (Ref. 3)	$Fe(H_2O)_6^{3+}$ (Ref. 5)	Calc. $Dq=1350$	beryl (Ref. 3)	Calc. $Dq=1400$	$MgO:Fe^{3+}$ (Ref. 3)	Calc. $Dq=1500$
12500	12600	13164	12300	12677	12100	11702
18000	17200	18015	17500	17575	(15000)	16683
(19000)					18000	
24599	24500	24849	23600	24849	25500	24849
27500		26752	26800	26735		26705
		28700		28700		28700
(b) Zero-field splitting $10^3(3a)$						
35	35	34.4	45	41	61.5	60.2

TABLE II. The comparison of our results for $3a$ with those of LR, in units of cm^{-1}.

B	730	730	1100	1100
C	3150	3150	4000	4000
α	90	90	90	0
ζ	300	420	440	440
Dq	1350	1350	2150	2150
$10^3(3a)$				
This paper	8.5	34.4	56.6	79.7
LR	3	16	22	29

Johnston[2] (PGJ); the calculated results are given in Table III. It is surprising to note that in order for us to obtain the same values of $3a$ the negative of their Dq has to be employed, that is to say, if we replace Dq by $-Dq$ in the calculations of PGJ,[2] we obtain our result. Our definition of Dq in the calculations is the same as that given by Schafer and Gliemann;[6] it is positive for the octahedral $3d$ electron configuration. For clarity, we calculate the values of $3a$ for both positive and negative Dq; the results are given in Table IV. When comparing our result,[7] 53.6×10^{-3} cm^{-1}, with that of PGJ, we also find that the difference is only the sign of Dq. From Table IV we have

$$(3a)_{+Dq} > (3a)_{-Dq} .$$

This result was also reported by Du and Zhao[4] who treated this problem in the framework of a high-order perturbation method. We have drawn the following conclusions. (1) The ground-state zero-field splitting of the Fe^{3+} ion in a cubic field can be determined by considering the crystal-field spin-orbit-coupling mechanism. (2) The assumption of Low and Rosengarten is not reasonable for the Fe^{3+} ion. (3) For the $3d^5$ electron configuration we have $(3a)_{+Dq} > (3a)_{-Dq}$. (4) For the d^5 configuration, we can use either the electron term or the hole term; the signs of both Dq and ζ are positive for the electron term and negative for the hole term, and so the signs of both Dq and ζ are always the same for the octahedral configuration. If the same sign is used in the whole calculation, our results can be obtained.

TABLE III. The comparison of our results for $3a$ with those of PGJ[2], all numbers in units of cm^{-1}. Initial parameters $B=900$, $C=3300$, $\zeta=400$.

			With doublets[a]		
Dq	PGJ $10^4(3a)$	This paper $10^4(3a)$	Dq	PGJ $10^4(3a)$	This paper $10^4(3a)$
1200	80.2	117	−1200	117	80.2
1000	42.1	63.6	−1000	63.6	42.1
800	21.1	34.4	−800	34.4	21.1
600	9.45	17.7	−600	17.7	9.45
400	3.06	7.85	−400	7.86	3.06
200	0.178	0.24	−200	0.24	0.178

[a]See Ref. 2.

TABLE IV. The comparison between the calculated results for $3a$ for positive and negative Dq, all numbers in units of cm^{-1}.

B	730		730		1100		1100	
C	3150		3150		4000		4000	
α	90		90		90		0	
ζ	300		420		440		440	
Dq	1350	−1350	1350	−1350	2150	−2150	2150	−2150
$10^3(3a)$	8.5	6.37	34.4	18.3	56.6	39.3	79.7	53.6

[1]H. Watanabe, Prog. Theor. Phys. Jpn. **18**, 405 (1957); Phys. Rev. Lett. **4**, 410 (1960).
[2]M. J. D. Powell, J. R. Gabriel, and D. F. Johnston, Phys. Rev. Lett. **5**, 145 (1960); Proc. R. Soc. London **264**, 503 (1961).
[3]W. Low and G. Rosengarten, in *Paramagnetic Resonance,* edited by W. Low (Academic, New York, 1963), p. 314; J. Mol. Spectrosc. **12**, 319 (1964).
[4]M. L. Du and M. G. Zhao, J. Phys. C **18**, 3241 (1985).
[5]O. G. Holmes and N. S. McClure, Chem. Phys. **26**, 1688 (1957).
[6]H. L. Schlafer and G. Gliemann, *Basic Principles of Ligand Field Theory* (Wiley, New York, 1970), p. 340.
[7]See Table IV in this paper and in Ref. 3.