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Analysis of temperature-dependent electron-paramagnetic-resonance spectra for *S*-state ions in MgO

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The relationship between the EPR cubic-field parameter $10^4(a)$, the covalence factor N, and the crystal-field strength Dq has been established by diagonalizing the complete matrices for ligand-field and spin-orbit coupling. A general method for calculating the local thermal-expansion coefficient of the impurity ion has been proposed. It is shown that the experiment of Rubio and Medrano is in agreement with the infrared and Raman spectra.

The EPR spectra of d^5 configuration ions have been widely studied theoretically and experimentally. In our previous works,[1-3] we have carried out the calculation of optical and EPR spectra for Fe^{3+} and Mn^{2+} in some crystals with six parameters B, C, α, β, ζ, and Dq, and our results have been confirmed by recent works.[4-7] However, up to now, there has been no theoretical study to interpret Rubio's experiment, which consists in measuring the effect of temperatuare on EPR spectra.[8] Indeed, as Rubio pointed out, it is very difficult to test any theory of the crystalline-field effect, until accurate estimates of the Racah, spin-orbit, spin-spin, and cubic-field parameters for these ions are made. In the following, a reasonable explanation about the Rubio's experiment has been given.

The Hamiltonian for d^5 configuration ions in a cubic crystal field can be written as[9]

$$\hat{H}=\hat{H}_{\text{atomic}}+\hat{V}_{\text{cubic}}+\hat{H}_{\text{s.o.}} . \tag{1}$$

The energy-level positions are functions of six parameters: B, C, α, β, ζ, and Dq. According to Curie's covalence theory, the five parameters, B, C, α, β, and ζ, depend on the free-ion parameters B_0, C_0, α_0, β_0, and ζ_0. By using the average covalency parameter[10] N, we have

$$\begin{aligned} &B=N^4B_0 , \quad C=N^4C_0 , \quad \alpha=N^4\alpha_0 , \\ &\beta=N^4\beta_0 , \quad \zeta=N^2\zeta_0 . \end{aligned} \tag{2}$$

The free-ion parameters[11-12] for Fe^{3+} and Mn^{2+} are those determined by using the method of Curie, Barthon, and Canny[10] and their values are listed in Table I. Then as far as we find the values of N and Dq for Fe^{3+} and Mn^{2+} in crystals, we can determine all energy-level splittings. In Tables II and III, we list the calculated results about the important energy levels $^4A(G)$, $^4G(G)$, $^4T_1(G)$ and the cubic EPR parameter $10^4(a)$, as a function of N and Dq. Employing a least-squares minimization procedure,[13] we obtain the explicit expression for $10^4(a)$,

$$10^4(a)=\sum_n C_n(dN^{-p})^n , \tag{3}$$

where $d=10^{-3}Dq$, C_n are constants and listed in Table IV, $p=4.6$ and 5.1 for Fe^{3+} and Mn^{2+}, respectively. From the formula (3), we can easily research the temperature-dependent EPR spectra for Fe^{3+} and Mn^{2+} in MgO.

The effect of temperature on EPR spectra for Fe^{3+} and Mn^{2+} in MgO had been measured by Rubio and Medrano[8] and Walsh.[14] Rubio and Medrano discovered that the temperature-dependent EPR spectra for Fe^{3+} in MgO are quite different from that of MgO:Mn^{2+}, and they believed that this result was very difficult to understand. We here report our theoretical interpretation.

The optical spectra and EPR spectra for Fe^{3+} and Mn^{2+} in MgO have been measured by Koidl and Blazey,[15] Blazey,[16] Low,[17] Walsh,[14] and Rubio and Medrano.[8] From their experimental data we find the average covalency parameter N and the crystal-field strength parameter Dq (for $T=293$ K), which are

$$\begin{aligned} &N=0.910 , \quad Dq=1316 \text{ cm}^{-1} \quad \text{for } Fe^{3+} \text{ in MgO} , \\ &N=0.965 , \quad Dq=995 \text{ cm}^{-1} \quad \text{for } Mn^{2+} \text{ in MgO} . \end{aligned} \tag{4}$$

The effect of temperature on the EPR spectra of Fe^{3+} and Mn^{2+} in magnesium oxide is associated with the local linear thermal-expansion coefficient[18]

TABLE I. The free-ion parameters B_0, C_0, α_0, β_0, and ζ_0 for Fe^{3+} and Mn^{2+}, in units of cm^{-1}.

	B_0	C_0	α_0	β_0	ζ_0
Fe^{3+}	1106	3922	81	−29	470
Mn^{2+}	918	3273	65	−131	347

TABLE II. The cubic ZFS parameter $10^4(a)$ and Stark levels ${}^4T_1(G)$, ${}^4A_1(G)$, ${}^4E(G)$ for Fe^{3+} as a function of N and Dq. All numbers are in units of cm^{-1}.

N	0.95	0.94	0.93	0.92	0.91	0.90
			${}^4A_1(G)$ ${}^4E(G)$			
	26 300	25 210	24 155	23 132	22 143	21 185
Dq			${}^4T_1(G)$			
1600	12 234	11 080	9 962	8 879	7 829	6 813
1400	14 178	13 027	11 912	10 831	9 784	8 770
1200	16 112	14 964	13 852	12 774	11 730	10 719
1000	18 033	16 889	15 780	14 705	13 664	12 657
700	20 877	19 740	18 637	17 568	16 534	15 532
500	22 731	21 599	20 503	19 440	18 410	17 414
300	24 507	23 385	22 297	21 243	20 223	19 234
			$10^4(a)$			
1600	195.3	271.0	391.2	599.4	1 001.3	1 933.0
1400	95.4	122.6	161.2	217.5	303.7	443.3
1200	50.5	62.1	77.2	97.4	125.2	164.1
1000	27.7	33.0	39.6	48.0	58.7	72.6
700	11.0	12.7	14.7	17.2	20.1	23.7
500	5.4	6.1	7.0	8.0	9.3	10.7
300	2.1	2.4	2.7	3.1	3.5	4.0
−300	0.5	0.6	0.7	0.8	0.9	1.1
−500	2.4	2.7	3.2	3.7	4.3	5.1
−700	6.1	7.1	8.3	9.7	11.5	13.6
−1000	17.7	21.1	25.4	30.7	37.5	46.3
−1200	33.6	41.2	51.0	63.9	81.4	105.3
−1400	64.3	81.9	106.1	140.5	191.1	268.6
−1600	129.5	175.1	244.5	355.5	545.5	899.2

TABLE III. The cubic ZFS parameter $10^4(a)$ and Stark levels ${}^4T_1(G)$, ${}^4A_1(G)$, ${}^4E(G)$ for Mn^{2+} as a function of N and Dq. All numbers are in units of cm^{-1}.

N	1.00	0.99	0.98	0.97	0.96	0.95
			${}^4A_1(G)$,${}^4E(G)$			
	26 845	25 787	24 761	23 766	22 801	21 865
Dq			${}^4T_1(G)$			
1400	14 684	13 575	12 493	11 443	10 425	9 437
1200	16 623	15 511	14 433	13 386	12 370	11 385
1100	17 585	16 475	15 398	14 353	13 338	12 355
1000	18 544	17 436	16 360	15 316	14 304	13 321
700	21 389	20 287	19 217	18 179	17 172	16 195
500	23 244	22 148	21 084	20 051	19 049	18 077
300	25 025	23 938	22 882	21 857	20 863	19 899
			$10^4(a)$			
1400	35.6	44.9	57.5	75.3	101.2	140.5
1200	19.2	23.3	28.5	35.2	44.3	56.5
1100	14.3	17.1	20.5	24.8	30.5	37.9
1000	10.7	12.6	15.6	17.8	21.4	26.0
700	4.2	4.9	5.6	6.5	7.5	8.8
500	2.1	2.3	2.7	3.0	3.5	4.0
300	0.8	0.9	1.0	1.1	1.3	1.5
−300	0.3	0.3	0.4	0.4	0.5	0.5
−500	1.1	1.2	1.4	1.6	1.9	2.2
−700	2.6	3.0	3.5	4.1	4.8	5.6
−1000	7.4	8.8	10.4	12.4	14.9	18.2
−1100	10.1	12.1	14.6	17.7	21.6	26.7
−1200	13.9	16.7	20.4	25.2	31.4	39.8
−1400	26.0	32.6	41.4	53.5	70.8	96.1

TABLE IV. (a) The values of C_n for Fe^{3+}. (b) The values of C_n for Mn^{2+}.

n	C_n	n	C_n
	(a)		
1	0.787	9	−7.612
2	9.359	10	−1.709
3	10.96	11	1.833
4	3.671	12	0.4433
5	−19.64	13	−0.2259
6	−3.104	14	−0.05808
7	17.15	15	0.01132
8	3.645	16	−0.003172
	(b)		
1	0.5809		
2	5.432		
3	1.992		
4	3.953		
5	−1.273		
6	−0.9023		
7	0.5209		
8	0.7503		

$$\alpha=\left[\frac{1}{L_{293}}\right]\left[\frac{dL}{dT}\right], \tag{5}$$

where L_{293} is the bond length at 293 K. By using the formula (3), the point-charge model and ignoring the change of parameter N, we get

$$\frac{\partial \ln a}{\partial T}=(1/a)\left[\frac{\partial a}{\partial d}\right]\left[\frac{\partial d}{\partial L}\right]\left[\frac{\partial L}{\partial T}\right], \tag{6}$$

where

$$\frac{\partial a}{\partial d}=(10^{-4}/d)\sum_n nC_n(dN^{-p})^n ,$$

$$\frac{\partial d}{\partial L}=-5d/L ,$$

$$\frac{\partial L}{\partial T}=\alpha L_{293} ,$$

$$L=L_{293}\left[1+\int_{293\text{ K}}^{T}\alpha\, dT\right] ,$$

$$d=d_{293}\Big/\left[1+\int_{293\text{ K}}^{T}\alpha\, dT\right]^5 .$$

Then

$$\frac{\partial \ln a}{\partial T}=-5\left[\frac{\alpha}{1+\int_{293\text{ K}}^{T}\alpha\, dT}\right]\left[\frac{\sum_n nC_n(dN^{-p})^n}{\sum_n C_n(dN^{-p})^n}\right]. \tag{7}$$

TABLE V. The local linear thermal expansion coefficients $\alpha_2=0.6116\alpha_1$ for MgO:Fe^{3+} and $\alpha_2=0.676\alpha_1$ for MgO:Mn^{2+}, in units of 10^{-6} K^{-1}. Here $\alpha_1=10^{-6}(-6.634+0.1064T-2.062\times10^{-4}T^2+1.417\times10^{-7}T^3)$ for perfect MgO in the temperature range 293–600 K.

T (K)	293	373	473	573
α_2(MgO:Fe^{3+})	6.36	7.16	7.71	8.13
α_2(MgO:Mn^{2+})	7.03	7.91	8.52	8.99

As long as we know the local linear thermal expansion coefficient α of MgO:Fe^{3+}, and MgO:Mn^{2+} systems, we can calculate the value of $\partial \ln a/\partial T$.

The local linear thermal expansion coefficient α such as Fe^{3+},Cr^{3+} in alums and Mn^{2+} in KZnF had been studied by Buscher and Lehmann[19] and Rodriguez and Moreno.[20] Buscher and Lehmann remarked that the determination of the true local geometries for impurity ions in the case of valence and/or size mismatch is still a challenging problem. Rodriguez and Moreno pointed out that the local thermal expansion around an impurity can be quite different from that of a perfect lattice. We here report a general method to calculate the local linear thermal expansion coefficient.

According to the physical requirement, the cation impurity in crystal must be in force equilibrium, as illustrated in the following:

$$Mg^{2+}\xleftarrow{F_1} O^{2-} \xrightarrow{F_2} M^{n+} ,$$

where M^{n+} represents the cation impurity ion Fe^{3+} or Mn^{2+}. The vibration of two nuclei in a diatomic molecule can be reduced to the motion of a single particle of mass u:

$$u=\frac{m_1m_2}{m_1+m_2} . \tag{8}$$

The system represents a harmonic oscillator, and potential energy is simply given by

$$V=\tfrac{1}{2}Kq^2 . \tag{9}$$

Here K is the force constant and $\mathbf{q}$ is the displacement from its equilibrium position. In arbitrary temperature, the force equilibrium must be satisfied, we have

$$\mathbf{F}_1+\mathbf{F}_2=0 , \tag{10}$$

where

$$\mathbf{F}_1=K_1\mathbf{q}_1 , \quad \mathbf{F}_2=K_2\mathbf{q}_2$$

and

$$\mathbf{q}=\mathbf{L}-\mathbf{L}_{293\text{ K}} .$$

K can be used to determine the local thermal expansion coefficient. The relationship between K and vibrational frequency $\tilde{\nu}$ is

$$\tilde{\nu}=\frac{1}{2\pi c}\sqrt{K/\mu} .$$

Therefore,

$$K=(2\pi c)^2u\tilde{\nu}^2 . \tag{11}$$

From formulas (10) and (11), we can establish the relationship between the local thermal expansion coefficient and that of perfect crystal (MgO),

$$\alpha_2=(u_1/u_2)(\tilde{\nu}_1/\tilde{\nu}_2)^2\alpha_1 . \tag{12}$$

The vibrational frequences for Mg-O, Mn-O, and Fe-O have been measured by infared and Raman technology, and the results have been summed by Nakamoto.[21] The

TABLE VI. The comparison of the calculated results of $\partial \ln a/\partial T$ for MgO:Fe^{3+} and MgO:Mn^{2+} with those of experimental data. All values of $\partial \ln a/\partial T$ are in units of 10^{-4} K^{-1}.

Temperature	293	373	473	573
		MgO:Fe^{3+}		
Calc.				
$10^4(a)$	203.4	200.0	195.6	191.0
$\partial \ln a/\partial T$	-1.936	-2.17	-2.30	-2.41
Expt.				
$10^4(a)$	203.8[a]			
$\partial \ln a/\partial T$	$-2.2(3)$[b]	$-2.2(3)$	$-2.2(3)$	$-2.2(3)$
		MgO:Mn^{2+}		
Calc.				
$10^4(a)$	19.02	18.83	18.57	18.30
$\partial \ln a/\partial T$	-1.19	-1.34	-1.43	-1.50
Expt.				
$10^4(a)$	19.01[a]			
$\partial \ln a/\partial T$	$-1.6(3)$[b]	$-1.6(3)$	$-1.6(3)$	$-1.6(3)$

[a] See Ref. 14.

[b] See Ref. 8.

linear thermal-expansion coefficient α_1 for perfect MgO has been reported by Kirby, Hahn, and Rathrock.[18] By employing formula (12) we have determined the local thermal expansion coefficients $\alpha_2=0.6116\alpha_1$ for Fe^{3+} in MgO and $\alpha_2=0.676\alpha_1$ for Mn^{2+} in MgO, respectively (see Table V). We note that the local thermal expansion coefficients of Fe^{3+} and Mn^{2+} in MgO are indeed very different from that of perfect MgO, and the reductions are 30–40%. This result is in accord with the conclusion of Rodriguez and Moreno.[20] Substituting the local thermal expansion coefficients into formula (7) we have obtained the theoretical values of $\partial \ln a/\partial T$ in the temperature range (293–600 K) for Fe^{3+} and Mn^{2+} in MgO, respectively. As shown in Table VI our data are in good agreement with the findings of Rubio and Medrano. This implies that the temperature-dependent EPR spectra for Fe^{3+} and Mn^{2+} in MgO is consistent with the infared and Raman spectra.

We can draw the following conclusions. (1) A general relationship between the EPR cubic parameter $10^4(a)$ and N and Dq has been established by using the Curie covalence theory and the ligand field theory. (2) A general method for calculating the local thermal expansion coefficient has been proposed. (3) We have verified that the experiment of Rubio and Medrano of the temperature-dependent EPR for Fe^{3+} and Mn^{2+} in magnesium oxide is in accord with the infared and Raman experiments.

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