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Two-center transitions in the antiferromagnetic salt $FeCO_3$

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The optical-absorption spectrum of the antiferromagnetic salt $FeCO_3$ has been measured. As many as 34 bands have been observed. In order to give a reasonable explanation of the observed spectrum, an *ab initio*—like calculation including a trigonal crystal field has been made. Three stronger bands at 24 390, 24 875, and 25 126 cm^{-1} are interpreted in terms of two-center transitions of Fe^{2+}-ion pairs. The essential idea is the application of an analytical approximation of Watson's self-consistent-field procedure to obtain the spin-orbit interaction and the electrostatic parameters for the isolated ions. Crystal-field energy levels are then calculated using the nearest-neighbor point-ion approximation. Despite these approximations, the results are quite good.

I. INTRODUCTION

Iron carbonate (occurring naturally as the mineral siderite) has a rhombohedral structure belonging to the space group D_{3d}^6 ($R\bar{3}c$). The Fe^{2+} ions order antiferromagnetically at 38 K in alternating (001) ferromagnetic sheets with the spin directed along the trigonal (c) axis. Neutron inelastic scattering studies demonstrate that the antiferromagnetic $FeCO_3$ is accurately described by the Ising model.[1] The Ising nature of the magnetic structure of $FeCO_3$ is a result of the crystal-field splitting of the Fe^{2+} ion as described by Kanamori and Okiji.[2] However, at the present time there is no satisfactory theory of a d-d transition in transition-metal ions which relates its spectrum to its crystal structure; consequently, a theoretical prediction of crystal-field splitting of a complex ion is not available. Recently an attempt was made using an *ab initio*—like calculation for the spectra of MnF_2 (Refs. 3—6) and ruby. In the present work we will investigate the quantitative relationship between spectra and crystalline parameters on the basis of an analytical approximation of Watson's self-consistent-field (SCF) d orbit. A specimen from the Sichuan siderite deposit was used in the present study.

II. d ORBIT FOR THE Fe^{2+} ION

Following the previous work,[3—6] and using three mathematical conditions governing overlap: $R_d(r) \approx R_d'(r)$ (Watson) ($r<0.4$ a.u.), $\langle R_d(r) | R_d' \rangle \approx 1$, and $\langle R_d | r^{-3} | R_d \rangle \approx \langle R_d' | r^{-3} | R_d'$ (Watson)$\rangle$, then the analytical approximation of Watson's SCF d orbit is approximately given by

$$R_d(r)=0.5692\left[\frac{11.038\,06^7}{6!}\right]^{1/2} r^2\exp(-5.519\,03r)+0.6500\left[\frac{3.547\,94^7}{6!}\right]^{1/2} r^2\exp(-1.773\,97r)\;.$$

Here the d orbit $R_d(r)$ is a solution of the Schrödinger equation,

$$\left[-\frac{1}{2}\frac{d^2}{dr^2}+\frac{3}{r^2}-v(r)-E\right]rR_d(r)=0\;,$$

with

$$v(r)=\left[\frac{3}{r}\right]\frac{a_1N_1\zeta_1\exp(-\zeta_1 r)+a_2N_2\zeta_2\exp(-\zeta_2 r)}{a_1N_1\exp(-\zeta_1 r)+a_2N_2\exp(-\zeta_2 r)}-\frac{1}{2}\frac{a_1N_1\zeta_1^2\exp(-\zeta_1 r)+a_2N_2\zeta_2^2\exp(-\zeta_2 r)}{a_1N_1\exp(-\zeta_1 r)+a_2N_2\exp(-\zeta_2 r)}-E\;,$$

$$N_j=\left[\frac{(2\zeta_j)^7}{6!}\right]^{1/2}\;,\quad j=1,2$$

$$a_1=0.5692,\quad a_2=0.6500,\quad \zeta_1=5.519\,03,\quad \zeta_2=1.773\,97\;,$$

where the potential $v(r)$ is an analytical approximation of the Hartree-Fock SCF central potential by Watson.[7] In the wave equation, the effects of s,p,d hybridization are neglected on the basis of the justification by Gray and Ballhausen.[8]

Using an IBM-130 computer and the formulas in Refs. 3—6, we find

$$\begin{aligned}
&\langle r^2\rangle=2.2949\;,\\
&\langle r^{-3}\rangle=4.6072\;,\\
&\langle r^4\rangle=14\;,\\
&\zeta_d=416\;,\\
&A=160\,830\;,\\
&B=947\;,\\
&C=3375\;,
\end{aligned}\qquad (2)$$

TABLE I. The energy levels of the free Fe^{2+} ion.

Term	j	Theoretical frequency (cm^{-1}) $\alpha=86\ cm^{-1}$ (Refs. 13 and 14)	Experimental frequency (cm^{-1}) (Ref. 15)
^5D_j	4	0	0
	3	416	436
	2	728	738.9
	1	936	932.4
	0	1 040	1 027.3
^3P_j	2	19 580	19 404.8
	1	19 788	20 688.4
	0	19 892	21 208.5
^3H_j	6	19 811	20 051.1
	5	20 335	20 300.8
	4	21 010	20 481.9
^3F_j	4	19 764	21 462.2
	3	20 180	21 699.9
	2	20 490	21 857.2
^3G_j	5	22 810	24 558.8
	4	23 331	24 940.9
	3	23 747	25 142.4

where $\langle r^2\rangle$, $\langle r^{-3}\rangle$, and $\langle r^4\rangle$ are in atomic units, and ζ_d, A, B, and C are in units of cm^{-1}. A, B, and C are the Racah electrostatic parameters, and ζ_d is the spin-orbit coefficient including the Blume-Watson[9] correction. A comparison of the theory with experiments is presented in Table I.

III. HAMILTONIAN MATRICES OF A $d^{4,6}$ CONFIGURATION POSSESSING C_{3v} SYMMETRY

In the work by Phillips,[10] a new method is presented for calculating crystal-field splittings. The method includes the effect of orthogonalization to ligand orbitals by grouping the latter terms into an effective repulsive potential. It is shown by a very general argument that this repulsive potential should cancel to high accuracy the excess attractive potential obtained when point-ion ligands are replaced by distributed-charge ligands. This result therefore provides a qualitative justification for the empirical success of the Van Vleck point-ion approximation for crystal fields. In this work we are utilizing the Van Vleck point-ion approximation for crystal-field energy levels.

In the case of C_{3v} symmetry, the crystal-field potential is given by

$$v=\sum_{i=1}^{N}\Bigg[-3\left[\frac{\pi}{5}\right]^{1/2} eqr_i^2\left[\frac{1}{R^3}(3\cos^2\Theta-1)+\frac{1}{R'^3}(3\cos^2\Theta'-1)\right]Z_{20}(\theta_i,\varphi_i)$$
$$-\frac{\sqrt{\pi}}{4}eqr_i^4\left[\frac{1}{R^5}(35\cos^4\Theta-30\cos^2\Theta+3)+\frac{1}{R^5}(35\cos^4\Theta'-30\cos^2\Theta'+3)\right]Z_{40}(\theta_i,\varphi_i)$$
$$-\frac{\sqrt{70\pi}}{2}eqr_i^4\left[\frac{1}{R^5}\sin^3\Theta\cos\Theta-\frac{1}{R^5}\sin^3\Theta'\cos\Theta'\right]Z_{43}^{c}(\theta_i,\varphi_i)\Bigg]\quad(C_3\|Z)\ ,$$

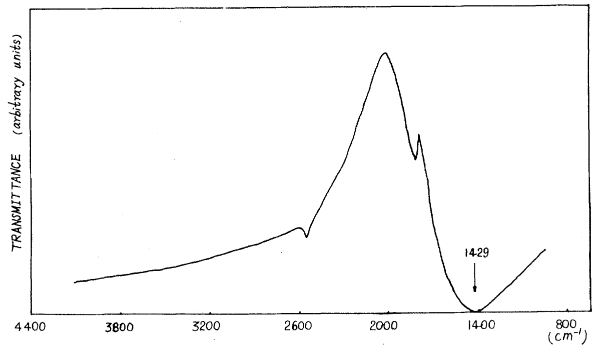

FIG. 1. Optical-absorption spectrum of siderite (800—4400 cm^{-1}).

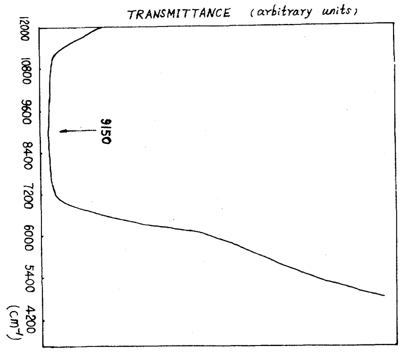

FIG. 2. Optical-absorption spectrum of siderite (4200—12 000 cm^{-1}).

TABLE II. *d-d* transition in $FeCO_3$.

Transition	Theoretical frequency (cm^{-1}) ($\alpha=85$ cm^{-1})[a] ($R=2.18$ Å, $\Theta=53.036°$) (Refs. 16 and 17)	Experimental frequency (cm^{-1})	
		This work	Refs. 1 and 2
$^5E(1)\rightarrow$ $^5A_1(1)$	1358	1429	1410
$^5E(2)$	9178	9150	10 000
$^3E(1)$	12 102	12 195	
$^3A_2(1)$	12 553	12 468	
$^3A_1(1)$	15 425	15 576	
$^3E(2)$	16 383	16 393	
$^3A_2(2)$	19 726	19 531	
$^3E(3)$	20 292	20 534, 20 833	
$^3E(4)$	21 591	21 186, 21 367	
$^3A_2(3)$	21 902	21 930	
$^3A_1(2)$	22 640	22 222	
$^3E(5)$	23 501	23 474	
$^3E(6)$	23 927	24 038	
$^3E(7)$	26 256	26 246	
$^3A_1(3)$	26 865	26 882	
$^3A_2(4)$	27 099	27 472, 27 777	
$^3E(8)$	29 029	28 736, 29 070	
$^3E(9)$	29 849	29 762	
$^3A_2(5)$	30 035	30 488	
$^3A_1(4)$	31 699	31 447	
$^3A_1(5)$	32 428	32 467	
$^3E(10)$	32 871		
$^3E(11)$	34 823		
$^3A_2(6)$	35 187	35 700	
$^3E(12)$	36 739	38 168	
$^3A_2(7)$	50 415	44 642?48 544?	
$^3E(13)$	50 446	50 000?	
$^3A_2(8)$	50 998	51 020?	
$^3E(14)$	53 532		
$^3A_1(6)$	54 870		
$^3A_2(9)$	55 671		
$^3E(15)$	56 918		
$^5E(1)+{}^5E(1)\rightarrow{}^3E(1)+{}^3E(1)$	24 204	24 390	
$^3E(1)+{}^3A_2(1)$	24 655	24 875	
$^3A_2(1)+{}^3A_2(1)$	25 106	25 126	

[a] α indicates Tree's correction.

where e is the electronic charge, q is the electric charge of ligand, (r_i,θ_i,φ_i) are the coordinates of the ith electron, (R_k,Θ_k,Φ_k) are the coordinates of the kth ligand, and $R=R'$, $\Theta'=\pi-\Theta$ for D_{3d} symmetry.

Until now, there were no complete ligand-field matrices of $d^{4,6}$ configuration possessing C_{3v} symmetry and including the Trees[11] correction. In this work, through elaborate mathematical derivations, the C_{3v} matrices of $d^{4,6}$ are derived using the weak-field scheme. The results are given in an unpublished paper.

IV. *d-d* TRANSITIONS OF $FeCO_3$

The optical-absorption spectrum of $FeCO_3$ is shown in Figs. 1 and 2; as many as 34 absorption bands have been observed in the Sichuan siderite. The stronger bands of 24 390, 24 875, and 25 126 cm^{-1} are interpreted in terms of the two-center transition of the Fe^{2+}-ion pairs (see Ref. 2). The comparison of theory with experiments is listed in Table II (see Figs. 1—3). In the calculation, the delocalization of the d orbitals are ignored on the basis of the experiments by Spiering *et al.*[12]

It follows from Table II that there is rather good numerical agreement between theory and experiment. This means that the errors of quite different sorts in the crystal-field model are compensated by the errors of the d orbit.

V. CONCLUSION

(a) Quantitative relationships between crystal-structure parameters and optical spectra are established with the use of an analytical approximation of Watson's SCF d orbit.

(b) For the *d-d* transitions in $FeCO_3$, there are no free parameters at all and no fitting of parameters to data has been done.

(c) This work presents an *ab initio*—like calculation of energy levels of the Fe^{2+} ion in $FeCO_3$. The essential idea

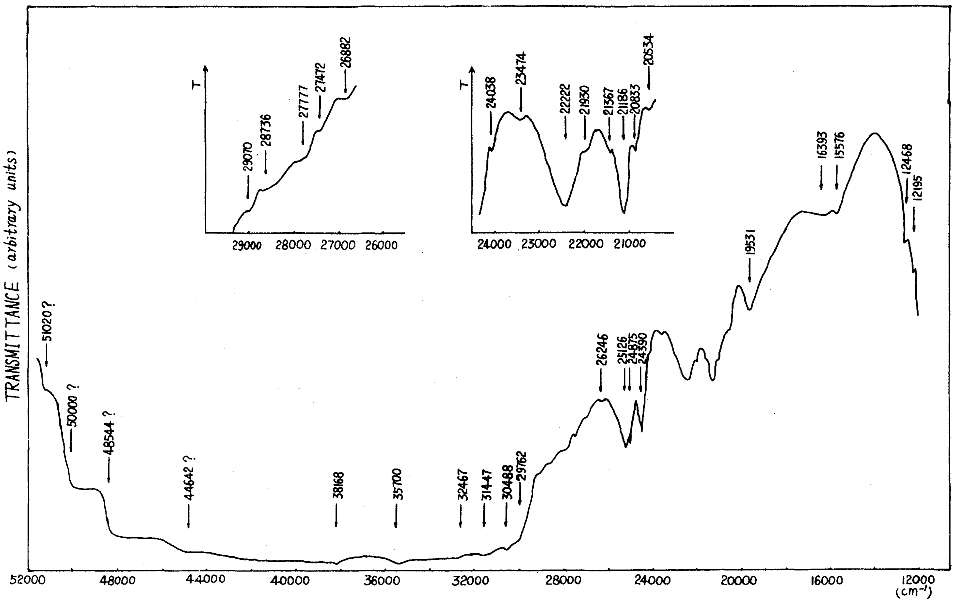

FIG. 3. Optical-absorption spectrum of siderite (12000—52000 cm^{-1}).

is the application of an analytical approximation of Watson's SCF procedure to obtain the spin-orbit interaction and the electrostatic parameters for the isolated ions. Crystal-field energy levels are then calculated using the nearest-neighbor point-ion approximation. Despite this approximation, the results are quite good, indicating that the technique may be of general use as the starting point of more sophisticated calculations on d^n ions in crystals.

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