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Ground-state splitting of antiferromagnetic $FeCO_3$

Zhou Yi-Yang
Chinese Center of Advanced Science and Technology (World Laboratory), P.O. Box 8370, Beijing 100080, People's Republic of China and Institute of Solid State Physics, Sichuan Normal University, Chengdu 610066, People's Republic of China

Yin Chun-Hao
Department of Physics, Xuzhou Teacher's College, Xuzhou 221009, People's Republic of China

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The ground-state splitting of antiferromagnetic $FeCO_3$, caused by a trigonal crystal field with spin-orbit and exchange interactions is studied with an energy-level scheme different from that proposed in previous papers. The present results on the infrared and Raman transitions, especially on bands that were not assigned in past works, are in good agreement with the experimental data. The difference between the present and previous schemes is discussed.

I. INTRODUCTION

Ferrous carbonate ($FeCO_3$) is a transparent antiferromagnet possessing strong uniaxial magnetic anisotropy,[1] which has been postulated to be an ideal Ising system.[2] Its magnetic properties arise predominantly from the effect of a cubic crystal field (CF) with a trigonal distortion and spin-orbit (SO) coupling in the ^5D ground state of the Fe^{2+} ion.[2] The magnetic excitations at low temperatures have been measured by neutron,[3,4] infrared,[5,6] and Raman[6–8] scattering, as well as by Mössbauer studies.[9–12] To investigate these excitations, the external magnetic field and the internal exchange interactions (EI) also have been considered (Refs. 2,4–6).

$FeCO_3$ has the rhombohedral calcite crystal structure with two molecules per unit cell.[13,14] The crystal field at the central ion Fe^{2+} is predominantly cubic, and this cubic component splits the free-ion ^5D ground state into an orbital doublet ^5E and a triplet $^5T_2$ separated by $\sim 10\,000$ cm^{-1}, with the triplet $^5T_2$ lying lowest.[1,11] The next-largest perturbation is the trigonal (C_{3V}) distortion (~ 1500 cm^{-1}), which separated the $^5T_2$ state into an orbital singlet $^5A_1$ and a doublet ^5E, which is the ground state (Refs. 1,15–17). The CF splitting scheme has been verified by Mössbauer studies.[9–12] However, to investigate additional splittings of the ground-state doublet ^5E due to the SO interaction, the following approximations were made in previous works. Introducing the Pauli spin matrix σ_z, Kanamori assumed the SO coupling energy in the ground-state doublet E to be $\lambda\langle L\rangle\sigma_z S_z$ ($\lambda\langle L\rangle=$constant, and $\sigma_z=\pm1$ with $S_z=\pm m$, $m=2,\ldots,-2$). Hence the ground-state doublet ^5E is further split into five equally spaced time-reversed pairs of degenerated states.[1,4,6] This splitting scheme ($S1$) is shown in Fig. 1. Neglecting the upper excited doublet ^5E because of a large separation ($\sim 10\,000$ cm^{-1}) between the ^5E and the $^5T_2$ states and considering the structural isomorphism between the $^5T_2$ and ^5P states, Griffth[15] treated the $^5T_2$ state as a ^5P state and expressed the wave functions in terms of $|M_S,M_L\rangle$ with $M_S=\pm2$, ±1, 0 and $M_L=\pm1,0$. In this splitting scheme ($S2$), shown in Fig. 1, the SO coupling splits the ground-state doublet ^5E into five doublets which are also equally split.[4–6] Using $S1$ and $S2$ and considering the EI, three allowed (two infrared and one Raman) transitions within the splittings of the ground-state doublet ^5E have been assigned.[4,5] As more infrared and Raman lines have been measured, Langille and O'Shea[6] have improved $S2$ with the $^5T_2$ wave functions still expressed in terms of the ^5P wave functions. In the improved scheme (IS2), shown in Fig. 1, the SO splitting levels from the ^5E ground state are not equally split. Unfortunately, they did not study quantitatively the EI splittings of the ground-state doublet ^5E, so that only one allowed Raman transition has been assigned within the splittings of the ^5E ground state. The above approximate treatment, especially the one that neglected the mixing of the ^5E and $^5T_2$ orbital states due to the trigonal CF and the SO interactions, can be seen frequently in the literature (Refs. 18 and 19).

It is well known that according to the standard group theory,[20–22] the SO interaction splits the ^5E state of the ^5D ($3d^6$ or $3d^4$) multiplet in the trigonal (e.g., C_{3V}) CF into seven separated states, four singlets and three doublets (e.g., $2A_1+2A_2+3E$ in C_{3V} symmetry; see also

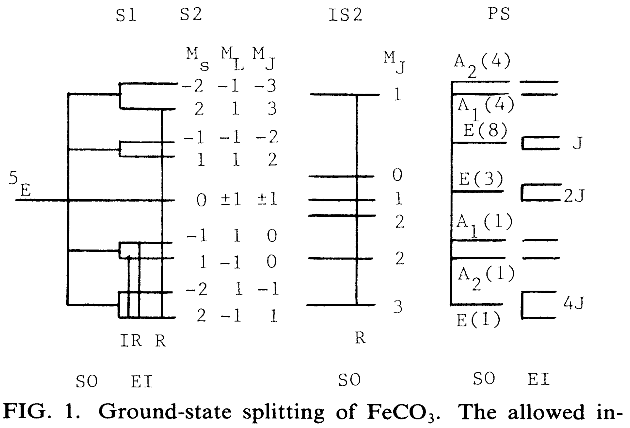

FIG. 1. Ground-state splitting of $FeCO_3$. The allowed infrared (IR) and Raman (R) transitions assigned in previous schemes ($S1$, $S2$, and IS2) are indicated. Each SO coupling level in the present scheme (PS) is a mix of states in the same irreducible representation; only the predominant component is indicated. The value of the EI splitting for the SO doublet is due to the predominant component.

Refs. 23–25), which will be discussed in detail. The present splitting scheme (PS), shown in Fig. 1, is very different from previous schemes. In this paper one can see that the theoretical results for the infrared and Raman transitions, calculated by using PS, are in good agreement with the experimental data.[4–6] In particular, the bands within the ground-state splittings of $FeCO_3$, which were not considered in past works, are assigned reasonably.

In addition, the difference between the present and the previous schemes for the ground-state splittings of $FeCO_3$ is discussed. More accurate calculation is indicated.

II. THEORY

A. Irreducible basis functions of the C_{3V} point group

According to Hund's rule, the ground state of the Fe^{2+} ($3d^6$) free ion is the ^5D multiplet with orbital momentum $L=2$ and spin $S=2$. The degeneracy of the ground level is then $(2L+1)(2S+1)=25$. To study the ground-state splitting of $FeCO_3$ simply and conveniently, it is natural to evaluate the 25×25 Hamiltonian matrix in a basis set of eigenfunctions for the irreducible representation of the C_{3V} point group. For this purpose, we need to know how the irreducible representation D_2^+ of the rotation group, corresponding to the total angular momentum $L=2$, breaks up into the irreducible representations of C_{3V}. Such a decomposition is given by the full-rotation-group compatibility table for the C_{3V} point group; for example, in Table 54 of Ref. 20:

$$D_2^+ \rightarrow 2E + A \ , \qquad (1)$$

in Mullikan's notations. One representation of E in Eq. (1) is issued from the $^5T_2$ state and the other from the ^5E state. The A representation in Eq. (1) is derived from the $^5T_2$ state. The introduction of the SO interaction into the Hamiltonian implies that we have to decompose the products of orbital and spin functions with $L=S=2$ into irreducible representations of C_{3V}. According to Eq. (1) and the relationship

$$E\times E = A_1 + A_2 + E \qquad (2)$$

quoted from the multiplication table of C_{3V} given in Table 50 of Ref. 20, we obtain

$$(2E+A)\times(2E+A) = 5A_1 + 4A_2 + 8E \ , \qquad (3)$$

where $2A_1+2A_2+3E$ is derived from the ^5E state and A_1+2E from the $^5A_1$ state. The relationship between the irreducible representation A_1, A_2 and E and the states $^5A_1$ and ^5E is shown in Table I. This shows clearly that the SO interaction splits the doublet ^5E of the ^5D multiplet in the trigonal CF into seven separated states, which is the same conclusion obtained recently from a set of theoretical studies of Fe^{2+} in C_{3V} symmetry.[23–25] Finally, using the projective operator method, the $|L=S=2,J,M_J\rangle$ basis functions of the irreducible representations of the C_{3V} point group are derived, as listed in Table I, where the functions $|S,L,J,M_J\rangle$ can be expressed in terms of $|S,L,M_S,M_L\rangle$ by the following general relationship:

$$|S,L,J,M_J\rangle = \sum_{M_S,M_L} C(S,L,M_S,M_L)|S,L,M_S,M_L\rangle \ , \qquad (4)$$

where $C(S,L,M_S,M_L)$ are the Clebsch-Gordan coefficients.

TABLE I. The $|L=S=2,J,M_J\rangle$ basis functions of the irreducible representations of the C_{3V} point group.

Irreducible representation	Basis function ($|J,M_J\rangle$)	State[a]
A_1	1 $(|4,3\rangle-|4,-3\rangle)\sqrt{2}$	$^5E_-$
	2 $(|3,3\rangle+|3,-3\rangle)/\sqrt{2}$	$^5E_+$
	3 $|4,0\rangle$	$^5A_1$
	4 $|2,0\rangle$	$^5E_-$
	5 $|0,0\rangle$	$^5E_+$
A_2	1 $(|4,3\rangle+|4,-3\rangle)/\sqrt{2}$	$^5E_-$
	2 $(|3,3\rangle-|3,-3\rangle)/\sqrt{2}$	$^5E_+$
	3 $|3,0\rangle$	$^5E_+$
	4 $|1,0\rangle$	$^5E_-$
$E_\pm$	1 $|4,\pm4\rangle$	$^5E_-$
	2 $|4,\mp2\rangle$	$^5A_1$
	3 $|3,\mp2\rangle$	$^5E_-$
	4 $|2,\mp2\rangle$	$^5E_+$
	5 $|4,\pm1\rangle$	$^5A_1$
	6 $|3,\pm1\rangle$	$^5E_+$
	7 $|2,\pm1\rangle$	$^5E_+$
	8 $|1,\pm1\rangle$	$^5E_-$

[a] $^5E_\pm$ correspond to the higher and lower energy state ^5E for the $3d^6$ ion, respectively, which should be the converse for the $3d^4$ ion.

B. Hamiltonian matrix

In crystals the magnetic ion is surrounded by other ions, giving rise to an electrostatic potential called the crystal field (CF). If the SO interaction is considered, the total Hamiltonian of the ion is[15–17]

$$H = H_{\mathrm{CF}} + H_{\mathrm{SO}} \ . \qquad (5)$$

The CF Hamiltonian within a ^{2S+1}L multiplet may be written

$$H_{\mathrm{CF}} = \sum_{K,q} B_K^q O_K^q(L_x,L_y,L_z) \ , \qquad (6)$$

where O_K^q are the extended Stevens operators.[26,27] The SO coupling can be expressed as

$$H_{\mathrm{SO}} = \lambda \mathbf{L}\cdot\mathbf{S} \ . \qquad (7)$$

According to the CF theory,[15,17] if the z and x (and y) axes are parallel and perpendicular to the trigonal axis, respectively, it is sufficient to consider the terms involving

$$B_2^0O_2^0, \ B_4^0O_4^0, \ B_4^3O_4^3 \qquad (8)$$

in the expression of the trigonal CF potential.[15–17,26,27] From Eqs. (7) and (8) and the irreducible basis function listed in Table I, we derive the Hamiltonian matrix (having dimensions of 5×5, 4×4, and 8×8 for the irreducible representations A_1, A_2, and E of point-group C_{3V}, respectively). The matrix elements are functions of the SO coupling constant λ and the CF parameters B_2^0, B_4^0, and B_4^3. It is easy to see that the energy levels caused by the trigonal CF and SO interactions can be obtained by diagonalizing this matrix as long as the CF parameters and SO coupling constants are known. It should be noted that each level obtained by diagonalizing this matrix corresponds to a mixing state of all states in the same irreducible representation shown in Table I, while the eigenfunction for each mixing state is obtained by diagonalizing this matrix. The state notation shown in Fig. 1 is the predominant component of the mixing state.

C. Exchange interaction

To explain the infrared and Raman spectra of $FeCO_3$, an appropriate Hamiltonian for an internal EI should be introduced.[1,4,5] If the Heisenberg form of the EI

$$H_{EI}=\sum_j J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j \tag{9}$$

is assumed, the EI Hamiltonian in an Ising system can be written, assuming $J_{ij}=J$ to be constant for all SO levels, as

$$H_{EI}=\sum_j JS_{iz}S_{jz} \ . \tag{10}$$

The EI leads to further splitting of the SO doublet. From Eqs. (4) and (10), it can be obtained, for example, that splitting of the doublet $|4,\pm 4\rangle$ is $4J$. The value of the EI splitting for each SO doublet, shown in Fig. 1, is caused by the predominant component of the mixing state mentioned above. Using Eq. (10) and the eigenfunctions obtained by diagonalizing the above Hamiltonian matrix, the EI splittings can be obtained provided the constant J is known.

III. RESULTS AND DISCUSSION

The present calculated results for the ground-state splittings of $FeCO_3$ are obtained, as listed in Table II, in the following sequence. Recently an *ab initio* calculation for $FeCO_3$ explained satisfactorily as many as 34 bands in the region of 800–52 000 cm^{-1} (Ref. 28). In the present calculation, we use the CF parameters $B_2^0=174.4$, $B_4^0=50.4$, and $B_4^3=1323.9$ cm^{-1} as was done in the *ab initio* calculation,[28] which makes the trigonal CF splittings (only the splittings of the ^5D state are shown in Table II) agree very well with the experimental data.[1,11,28] Using the SO coupling constant $\lambda=100$ cm^{-1} for Fe^{2+}, as usual,[1,4,5,11,15–19,23–28] the splittings of the ground-state doublet ^5E are obtained by diagonalizing the Hamiltonian matrix, as shown in Fig. 1 and listed in Table II. The notations of the irreducible basis functions [i.e., $A_1(n)$, $A_2(n)$, $E(n)$, e.g., $E(1)$] in Fig. 1 and Table II correspond to those of the predominant component of the mentioned mixing state (e.g., $|4,\pm 4\rangle$), which is given in Table I. The calculated results show qualitatively that the SO interaction splits the doublet ^5E of the ^5D multiplet in the trigonal CF into seven separated states. Finally, using the eigenfunctions obtained by diagonalizing the Hamiltonian matrix and taking the EI constant $J=9$ cm^{-1}, the ground-state splittings of $FeCO_3$ are obtained, as listed in Table II. The present results are in good agreement with the experimental data.[4–6] Not only the three (two infrared, 112 and 160 cm^{-1}, one Raman, 440 cm^{-1}) lines studied in previous papers[4,5] but also three additional lines not considered in previous works[4–6] are assigned as well.

TABLE II. Energy levels of $FeCO_3$ (in cm^{-1}).

Trigonal CF				+	SO		+	EX	
^5E	9180	9150[a]	10 000[b]						
$^5A_1$	1360	1430[a]	1 410[b]						
					$A_2(4)$	495		508	
					$A_1(4)$	494		507	504[e]
								391	440[c,d,e]
					$E(8)$	368		367	
								269	292[e]
^5E	0				$E(3)$	246		245	
					$A_1(1)$	138		151	160[c,d,e]
					$A_2(1)$	109		121	112[c,d,e]
								24	24[e]
					$E(1)$	0		0	0

[a] Reference 28.
[b] Reference 2.
[c] Reference 5.
[d] Reference 4.
[e] Reference 6.

Let us further discuss the difference between the present and the previous schemes. As mentioned above, the approximation in S1 and S2 yields ground-state splittings of $FeCO_3$ quite differently from those yielded in PS, where the ground-state splittings are caused by the SO and exchange interactions. Along with this, the following two differences have arisen: (a) The infrared and the Raman transitions are governed by the selection rules $\Delta M_J=\pm 1$, 0 for the former and $\Delta M_L=\pm 2$, ± 1, 0 and $\Delta M_S=0$ for the latter. Thus in *S*1 and *S*2, there is one allowed Raman transition from the ground state $|-2,1\rangle$ to the excited state $|-2,-1\rangle$ (Refs. 4,5) within the splittings of the ground-state doublet ^5E (Fig. 1). The other lines in *S*1 and *S*2 (Fig. 1) indicate the two allowed infrared transitions.[4,5] However, as mentioned above, the states in PS (Fig. 1) are mixed well enough so that the transitions from the ground state to all excited states split from the ground-state doublet ^5E are appreciable. It should be pointed out that the line 24 cm^{-1} measured by neutron scattering was assigned[4] to the Mn^{2+} impurities. However, the present results show that it should exist in pure $FeCO_3$. This needs to be identified further. (b) The splittings of the ground-state doublet ^5E are determined by the SO and exchange interactions. Five lines caused by the SO interaction in *S*1 and *S*2 were equidistant. To fit the experimental data, a strong EI ($J=19$ cm^{-1}) had to be introduced. However, in PS the SO coupling has split the ground-state doublet ^5E into seven unequally spaced lines so that there is a need of a weak EI ($J=9$ cm^{-1}). The value of the EI parameter J cannot be determined directly from either neutron-scattering measurements or infrared and Raman transition studies.[5,29–30]

Usually this has been evaluated[29–40] by fitting some measured data, e.g., $J=4$ cm^{-1} for Fe^{2+}-Fe^{2+} in FeF_2 (Ref. 30), obtained by fitting the transition temperature; $J=12$ cm^{-1} for Fe^{2+}-Fe^{2+} in K_2FeF_4 (Ref. 33), obtained by fitting the spin-wave energies, etc. However, there is a large difference between the empirical expressions used in previous works, e.g.,

$$kT_N/J = 4/[z\ln(1-2/z)]$$

$$kT_N/J = 5(z-1)[11S(S+1)-1]/192\ ,$$

where T_N is the transition temperature, z the number of nearest neighbors, and S the spin. The former[5] applies to Ising antiferromagnets and yields $J=16\ \text{cm}^{-1}$ in FeCO_3, close to that used in $S1$ and $S2$,[5] while the latter[30,31] applied to both Ising ferromagnets and antiferromagnets and yields $J=3\ \text{cm}^{-1}$ in FeCO_3, near to that in PS. The good agreement between the currently calculated and the measured infrared and Raman transitions indicates that a weak EI in FeCO_3 seems reasonable. It is significant to study the EI in FeCO_3 further, for the actual exchange interaction in this crystal has not been quite clear as yet.

The present calculation, based on the contribution of the upper excited doublet ^5E, yields very different results from previous works. The separation between the ground and the excited orbital doublets ^5E is about 10 000 cm^{-1}. Recently several lines ($\sim 12\,000\ \text{cm}^{-1}$) due to the transition $^3P \leftarrow {}^5D$ in FeCO_3 have been measured. The small difference between lines 10 000 and 12 000 cm^{-1} shows that the spin triplet ^3L ($L=P,D,F,G$, and H) should be considered in the study of the ground-state splittings of FeCO_3. This makes the Hamiltonian matrix have dimensions of 29×29, 25×25, and 53×53 for the irreducible representations A_1, A_2, and E of point group C_{3V}, respectively. Consequently, the splittings caused by the exchange interaction become more complex. Perhaps this is of interest to readers who want to obtain more accurate calculations for the ground-state splittings of FeCO_3.

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