PHYSICAL REVIEW B VOLUME 43, NUMBER 4 1 FEBRUARY 1991

Trigonal splitting of a ^6S-state ion

Wang Jun-Zhong
Institute of Solid State Physics, Sichuan Normal University, Chengdu 610066, People's Republic of China

Yu Wan-Lun
Center of Theoretical Physics, Chinese Center of Advanced Science and Technology (World Laboratory) and Department of Physics, Sichuan Normal University, Chengdu 610066, People's Republic of China

Fang Ke
Institute of Solid State Physics, Sichuan Normal University, Chengdu 610066, People's Republic of China

(Received 12 July 1990)

A very simple Γ_4 matrix of $D'_3(d^5)$ is derived and is applied to examine the perturbation procedures suggested for calculating the rank-two zero-field splitting of ^6S-state ions in trigonal symmetry. It is found that the Blume-Orbach procedure works badly in strongly distorted crystals and that the procedure proposed by Watanabe and developed by Yu and co-workers is always appropriate when the next-lowest order is taken into account. In Fe^{3+}:Al_2O_3, we find the spin-orbit mechanism is most important; the splitting comes mainly from the combination interaction of the spin-orbit coupling and the rank-four components of the crystal field.

I. INTRODUCTION

The zero-field splitting of ^6S-state ions has been extensively studied in the past decades (see Ref. 1). Among the various mechanisms[2-11] suggested to contribute to the splitting, the spin-orbit (SO) mechanism has been known to be most important for many substances and so has received great interest.[2-6,12-14] In addition to the perturbation procedure proposed by Blume and Orbach[2] and developed by Sharma, Orbach, and Das,[3] Yu and coworkers[6,12] have recently found that the methods suggested by Watanabe[5] and by Macfarlane[15] and Zdansky[16] can be developed to approach the splitting reasonably well. Although it was extensively adopted to analyze the electron-spin-resonance (ESR) data, the Blume-Orbach procedure was recently criticized as being incorrect.[14] On the other hand, Baur and Sharma[17] did not think that Watanabe's procedure was available. However, Yu and Zhao[1] have pointed out that all three distinctive procedures can reach results close to each other in the trigonal case. Diagonalizing the energy matrices provides the most appropriate approach to the splitting and so serves as a powerful tool for examining the perturbation procedures.

The present work derives the full-energy Γ_4 matrix of the D'_3 group for the d^5 configuration, considering the spin-orbit interaction, with the help of a new method suggested by Yu.[18] The calculation is rather simple, and the nonzero elements with a number less than 100 survive in the 34×34 Γ_4 matrix, which is useful in the calculation of the trigonal splitting of ^6S. This will be presented in Sec. II. Based on this matrix, we examine the Blume-Orbach and Watanabe perturbation procedures in Sec. III, called, respectively, SO-I and SO-II in Ref. 1 and in this paper hereafter. We find that, the SO-I is available only for weak distortion cases. The SO-II procedure is always correct even for strong distortion. Section IV will investigate the zero-field splitting of Fe^{3+} ions in Al_2O_3 crystals. We shall show the importance of the SO mechanism in this substance.

II. Γ_4 MATRIX OF $D'_3(d^5)$

The method used here in the derivation of the Γ_4-energy matrix of $D'_3(d^5)$ is quite different from that in the literature. In past works dealing with the spin-orbit splittings of ions in crystals, the basis functions of a double-valued group were chosen as linear combinations of the weak-field bases $|\alpha SLJM_J\rangle$, on which the spin-orbit couplings H_{so} is diagonal.[15,19,20] On the basis $|\alpha SLJM_J\rangle$, matrix elements of a crystal field V lie far from the diagonal line. Although it is very suitable for f^n ions, where $|\langle H_{so}\rangle| \gg |\langle V\rangle|$, this method is unsatisfactory in the case of $3d^n$ ions, where $|\langle H_{so}\rangle| \ll |\langle V\rangle|$ and where we prefer to consider the spin-orbit interaction splitting the crystal-field multiplets. To achieve this we have to choose a suitable set of basis functions on which the matrix elements of a crystal field lie as close to the diagonal line as possible.

As suggested by Yu,[18] we choose the basis functions of a double-valued group as the symmetry-adapted spin states $|S\Gamma_j\gamma_j\rangle$ coupled with the orbit states $|l^n\alpha SL\Gamma_i\gamma_i\rangle$ transforming symmetrically according to the corresponding point group:

$$|l^N\alpha SL\Gamma\gamma\rangle = \sum_{\Gamma_i,\gamma_i,\Gamma_j,\gamma_j} C(\Gamma_i\gamma_i\Gamma_j\gamma_j;\Gamma\gamma)|l^N\alpha SL\Gamma_i\gamma_i\rangle|S\Gamma_j\gamma_j\rangle \ , \tag{1}$$

where

$$|l^N\alpha SL\Gamma_i\gamma_i\rangle = \sum_{M_L} C(\Gamma_i\gamma_i M_L)|l^N\alpha SLM_L\rangle \ . \tag{2}$$

The C's are coupling coefficients. As the result of the fact that a crystal field is unrelated to spin, its matrix on the bases given in (1) is block diagonal, and the basic elements are given as

$$\langle l^N\alpha SLM_L|V|l^N\alpha' SL'M_L'\rangle = \sum_{k,q} B_{kg}\langle l\|C^{(k)}\|l\rangle(-1)^{L-M_L} \times \begin{bmatrix} L & k & L' \\ -M_L & q & M_L' \end{bmatrix} \langle l^N\alpha SL\|U^{(k)}\|l^N\alpha' SL'\rangle \ , \tag{3}$$

where V is written as

$$V = \sum_{k,q} B_{kq}C_q^{(k)} \ . \tag{4}$$

The elements of H_{so} are also easy to calculate and relate to the reduced matrix elements $\langle l^N\alpha SL\|V^{(11)}\|l^N\alpha' S'L'\rangle$, when Racah's irreducible tensor operator technique and group theory are fully applied. $\langle l^N\alpha SL\|V^{(11)}\|l^N\alpha' S'L'\rangle$ and $\langle l^N\alpha SL\|U^{(K)}\|\alpha' SL'\rangle$ can be found in Ref. 19.

In our case of Γ_4 of $D_3'(d^5)$, we omit the spin doublets for our special purpose (see Sec. III), and the dimension thus becomes 34×34. It is made of ${}^6A_1(|M_s|=\frac{1}{2}, i=1)$ ${}^6A_1$ $(|M_s|=\frac{5}{2}, i=2)$, ${}^4A_1$ $(i=3\text{–}6)$, ${}^4A_2$ $(i=7\text{–}10)$, ${}^4E$ $(i=11\text{–}18$, $19\text{–}26$, and $27\text{–}34)$, i denoting columns or rows. The matrix elements of the crystal field are displayed in Table I and those of the spin-orbit interaction in Table II. It is seen that although the dimension of the matrix is large (34×34), it has independent and nonzero elements less than 100. To use the matrix, one has to add it diagonally with the electrostatic elements:

$$H(i,i)=0 \quad \text{for } i=1,2 \ ,$$

$$H(i,i)=7B+7C+2\alpha+2\beta \quad \text{for } i=7,11,19,27 \ ,$$

$$H(i,i)=17B+5C+6\alpha \quad \text{for } i=3,12,13,20,21,28,29 \ ,$$

$$H(i,i)=22B+7C+12\alpha+2\beta \quad \text{for } i=4,8,9,14,15,22,23,30,31 \ ,$$

$$H(i,i)=10B+5C+20\alpha \quad \text{for } i=5,6,10,16\text{–}18,24\text{–}26,32\text{–}34 \ .$$

III. AXIAL TERM D

A. Negligibility of spin doublets

We will show that it is reasonable to omit the spin doublets in the diagonalized approach to D (or b_2^0). One might expect a more accurate result when taking the spin doublets into account than when omitting them, but it is not the case.

Denote the energy separation between $M_s=\pm\frac{5}{2}$ and $\pm\frac{1}{2}$ of ${}^6A_1$ with δ. It is easy to show that, to second order,

$$\delta/6 \approx D + \tfrac{1}{18}(a-F) - \tfrac{10}{81}\frac{a^2}{D} \ , \tag{5}$$

assuming D is much greater in magnitude than the rank-four splitting parameters a and F. So $D\approx\delta/6$ is reasonable, as has been adopted in Refs. 20–22, and has an accuracy $\frac{1}{18}|a-F|/|D|$, with numbers different from one crystal to another.

However, $D\approx\delta/6$ is not correct in the situation that D is comparable with or even less than a, in magnitude,

TABLE I. Nonzero matrix elements of a D_3 crystal field, $V_{ij}=aB_{20}+bB_{40}+cB_{43}$ (Γ_4: 34×34). For $i,j=19\text{–}26$, $V_{i,j}=V_{i-8,j-8}$, and for $i,j=27\text{–}34$, $V_{i,j}=V_{i-16,j-16}$.

i	j	a	b	c	i	j	a	b	c
3	4	0	0	$\frac{1}{7}\sqrt{10}$	12	14	$\frac{8}{35}\sqrt{10/7}$	$-\frac{10}{21}\sqrt{5/14}$	0
4	5	0	0	$\frac{5}{21}\sqrt{2}$		15	0	0	$-\frac{1}{21}\sqrt{5}$
	6	$\frac{3}{7}$	$-\frac{5}{21}$	0	13	14	0	0	$-\frac{5}{21}\sqrt{2}$
7	10	0	0	$\sqrt{2/7}$		15	$-\frac{8}{7}\sqrt{1/7}$	$-\frac{10}{21}\sqrt{1/7}$	0
8	10	0	0	$-\frac{1}{3}\sqrt{2/7}$	14	16	$\frac{3}{7}\sqrt{5/21}$	$\frac{1}{7}\sqrt{15/7}$	0
9	10	$\frac{3}{7}$	$-\frac{5}{21}$	0		17	0	0	$\frac{1}{7}\sqrt{2/3}$
11	12	$\sqrt{3/35}$	0	0		18	0	0	$-\sqrt{2/21}$
	16	0	$-\frac{1}{3}\sqrt{10/7}$	0	15	16	0	0	$\frac{1}{7}\sqrt{10/3}$
	17	0	0	$\frac{1}{3}$		17	$-\frac{12}{7}\sqrt{1/21}$	$-\frac{5}{7}\sqrt{1/21}$	0
	18	0	0	$-\frac{2}{3}\sqrt{1/7}$					

TABLE II. Nonzero matrix elements of the spin-orbit coupling H_{SO}, $H_{\mathrm{SO}}(i,j)=a\zeta_{nd}$, for Γ_4 representations (34×34).

i	j	a	i	j	a	i	j	a	i	j	a
1	7	$-\sqrt{3}$	4	34	$-\frac{2}{3}$	9	28	$-4\sqrt{1/21}$	21	30	$\frac{2}{7}\sqrt{14/15}$
	11	$-\frac{1}{2}\sqrt{2}$	5	8	$\frac{2}{3}\sqrt{1/7}$		33	$\frac{1}{3}\sqrt{1/7}$	22	24	$\frac{3}{2}\sqrt{5/21}$
	27	$-\frac{1}{2}\sqrt{6}$		14	$-\sqrt{1/7}$		34	$-\frac{2}{3}$		28	$-\frac{2}{7}\sqrt{14/15}$
2	19	$-\sqrt{5}$		30	$2\sqrt{1/21}$	10	15	$\frac{1}{2}$		33	$\frac{1}{2}\sqrt{10/7}$
3	7	$\frac{1}{3}\sqrt{7/5}$	6	9	$\frac{1}{6}$		31	$\sqrt{1/3}$	23	25	$3\sqrt{1/21}$
	8	$2\sqrt{1/35}$		15	$\frac{1}{2}$	11	12	$-\frac{3}{2}\sqrt{7/15}$		29	$4\sqrt{1/21}$
	11	$-\sqrt{7/30}$		31	$-\sqrt{1/3}$	12	14	$-8\sqrt{1/70}$		32	$-\frac{1}{2}\sqrt{2/7}$
	14	$4\sqrt{1/35}$	7	12	$-\sqrt{7/10}$	13	15	$-2\sqrt{1/7}$	24	31	$\frac{1}{2}\sqrt{2/7}$
	27	$\frac{1}{3}\sqrt{14/5}$		29	$-\sqrt{14/15}$	14	16	$-\frac{3}{2}\sqrt{5/21}$	25	30	$-\frac{1}{2}\sqrt{10/7}$
	30	$-\frac{8}{7}\sqrt{7/15}$	8	12	$4\sqrt{1/70}$	15	17	$-3\sqrt{1/21}$	27	29	$-\frac{1}{2}\sqrt{7/15}$
4	10	$\frac{1}{6}$		16	$-\sqrt{5/21}$	19	20	$\frac{3}{2}\sqrt{7/15}$	28	31	$-\frac{2}{3}\sqrt{1/7}$
	13	$-2\sqrt{1/7}$		29	$\frac{4}{7}\sqrt{14/15}$		28	$\sqrt{7/5}$	29	30	$-\frac{8}{3}\sqrt{1/70}$
	17	$\frac{1}{6}\sqrt{3/7}$		32	$-\frac{2}{3}\sqrt{5/7}$	20	22	$8\sqrt{1/70}$	30	32	$-\frac{1}{2}\sqrt{5/21}$
	18	$\sqrt{1/3}$	9	13	$-2\sqrt{1/7}$		31	$-4\sqrt{1/21}$	31	33	$-\sqrt{1/21}$
	28	$4\sqrt{1/21}$		17	$\frac{1}{6}\sqrt{3/7}$	21	23	$2\sqrt{1/7}$			
	33	$-\frac{1}{3}\sqrt{1/7}$		18	$-\sqrt{1/3}$		27	$-\sqrt{7/5}$			

which would happen in weakly distorted crystals. Actually, instead of (5), we have

$$|\delta|=\tfrac{1}{3}[(18D+a-F)^2+80a^2]^{1/2}\ . \tag{6}$$

Indeed, we cannot reduce D from the value of δ in such a case. To see this more plausibly, one notes the fact that $|\delta|\approx|3a|$ when $|a|\gg D$.

The cubic term a comes mainly from the spin doublets,[23–25] and so does the rank-four axial term F.[26] The above discussion leads us to the conclusion that when taking into account the spin doublets, the expression $D\approx\delta/6$ is applicable only in strongly distorted case and has an accuracy of usually 10^{-2} or less.

Physical considerations lead us to conclude that the spin doublets are negligible in affecting the rank-two axial term D. As a matter of fact, the doublet has a contribution to it at an order two or more higher than the lowest order in both perturbation procedures,[2–6] through the fourth- or higher-order interaction with the spin-orbit coupling. The contribution must be three or four orders less than that resulting from the spin quartets. Therefore, in the diagonalization calculation of D, the doublets are definitely negligible.

Including only the spin quartets, which contributes to a a value generally less than 10^{-4} cm^{-1},[23–25] (5) becomes

$$\delta/6\approx D-F/18\ , \tag{7}$$

to a fairly good approximation. In any case, $|F|/|D|\sim 10^{-2}$, according to the crystal-field model, taking into account the doublets or not.[26] Therefore, when omitting the doublets and using

$$\delta/6\approx D \tag{8}$$

to approach D, one can reach an accuracy of 10^{-3}.

We omit the doublets in our diagonalized approach to D.

B. Results

Tables III and IV show a comparison among the results calculated by diagonalization and by the SO-I and SO-II perturbation procedures. Table III displays D versus D_q, with $B_{20}=-1000$ cm^{-1} and $B'_{40}=1000$ cm^{-1} fixed ($B'_{40}=B_{40}\pm B_{43}\sqrt{7/10}$; see Ref. 1). SO-I was calculated in the lowest (third) order. Table IV shows the θ dependence of D in D_{3d} symmetry, having taken $\overline{A}_2=5500$ cm^{-1} and $\overline{A}_4=600$ cm^{-1}. D is found to be positive for compressed crystals $[\theta>\theta_c=\cos^{-1}(3^{-1/2})=54.735\,61°]$ and negative for elongated ones $(\theta<\theta_c)$. We have taken $B=911$, $C=3273$, $\alpha=65$, $\beta=-131$, and $\zeta=337$ cm^{-1} in both tables.

It is seen that SO-I and SO-II are both correct, supporting the conclusion made in Ref. 1. It is noted, however, that SO-I works badly for strongly elongated D_{3d} crystals (Table IV). This is to be expected, because it takes the value of the low-symmetric components of a field as a perturbation term.[2–4] When the components (B_{20} and B'_{40}) become large, in the strongly distorted case, this procedure will not be expected to work well. However, surprisingly, it is appropriate in the strongly compressed D_{3d} case, probably by chance.

The SO-II procedure always works well when the next order (sixth) is taken into account. Its lowest-order perturbation provides a good approximation when $|D_q|<1100$ cm^{-1}. Although the cubic component is tak-

TABLE III. D_q dependence of D in trigonal symmetry ($B'_{40}=1000$ cm^{-1}, $B_{20}=-1000$ cm^{-1}; D_q is in cm^{-1} and D in 10^{-4} cm^{-1}).

Dq	500	600	700	800	900	1000	1100	1200	1300	1400	1500
$D^{(4)}$ (SO-II)	66	77	88	99	111	122	133	144	155	166	177
$D^{(6)}$ (SO-II)	2	4	5	8	12	16	21	27	34	42	52
D (SO-II)	68	81	93	107	123	138	154	171	189	208	229
D (SO-I)	60	75	91	108	130	153	180	214	253	300	360
D (accurate)	69	82	96	110	126	143	162	182	205	231	262

en as a perturbation term, the procedure has a good convergency even when D_q reaches 1500 cm^{-1}, at which $D^{(4)}+D^{(6)}$ accounts for 87% of the total value of D. This thus removes the doubt expressed in Ref. 17 about this procedure, in which it was claimed that the cubic field as a perturbation term would break the convergency.

IV. Fe^{3+}:Al_2O_3

We now consider Fe^{3+}:Al_2O_3, which is strongly trigonally distorted.[27] We will show that the spin-orbit mechanism is most important in this substance.

Febbraro[21] and Kuang[22] considered the problem. Both the authors omitted all mechanisms except the SO one and used the point-charge model in dealing with the crystal field. In our calculation, we will adopt the superposition model[28] treating the crystal-field components and consider other mechanisms.

From the relationship between $\bar{A}_4$ and D_q,[1] we find $\bar{A}_4=1174.4$ cm^{-1} according to the optical measurement,[29] which gave $D_q=1510$ cm^{-1}, $B=660$ cm^{-1}, and $C=4.75B$. B'_{40} is consequently calculated to be 3940 cm^{-1} for $t_4=5$. $\bar{A}_2$ is much greater than $\bar{A}_4$,[28] and we take $\bar{A}_2=10.8\bar{A}_4=12\,684$ cm^{-1} according to Refs. 30 and 31; consequently, $B_{20}=1424$ cm^{-1} is obtained for $t_2=3$. ζ is found to be 380 cm^{-1} by the way of fitting the cubic term $a=236.6\times10^{-4}$ cm^{-1} (Ref. 32) with the reported optical data,[29] which is compared to $\zeta=368$ cm^{-1} used in Ref. 22 and 323 cm^{-1} in Ref. 21. We obtain D(SO)$=0.1935$ cm^{-1} by diagonalization. The covalency and overlap (CO) contribution is calculated to be -0.0359 cm^{-1}. Thus we have, as the total value of D,

$$D=+0.1576 \text{ cm}^{-1} ,$$

which is comparable with the experimental finding[32] $+0.1718$ cm^{-1}. Any of the other mechanisms, such as SS,[9] SS-SO,[6] and ODS (Ref. 10), are found to contribute a value of a few 10^{-4} cm^{-1} in magnitude and so are negligible.

With the same parameters, the SO-I perturbation procedure gives $D=0.3600$ cm^{-1}, while SO-II gives 0.1582 cm^{-1}. They are compared to the accurate value 0.1935 cm^{-1}. The case supports the conclusion made in Sec. III A.

$\bar{A}_2$ was considered to be a free parameter and taken to be $10.8\bar{A}_4=12684$ cm^{-1} in our calculation. This intrinsic parameter influences the calculated D a little: When $\bar{A}_2$ goes from 12 684 to 8000 cm^{-1}, D(SO) goes from 0.1935 to 0.2044 cm^{-1}. Because of this and since B'_{40} was determined from the experimental data on the crystal structure and D_q and ζ from the datum of a, we believe our result is reliable.

Nevertheless, B_{20} is small in Fe^{3+}:Al_2O_3. Its contribution to D is negligible. The splitting comes mainly from the rank-four crystal field B_{4q}, through the SO mechanism and from the quadrupole process.

The CO mechanism is the second important one in Fe^{3+}:Al_2O_3; it contributes negatively, with a magnitude 21% of the experimental value. It was omitted in Refs. 21 and 22, and so their the agreement obtained between theory and experiment is fortuitous.

The superposition model of the spin-Hamiltonian parameter of a ^6S-state ion[33] fails to account for the experimental data of Fe^{3+}:Al_2O_3. It was known $\bar{b}_2$ is negative for Fe^{3+}-O^{2-}.[34] Thus this model will lead to a negative value of D according to the crystal-structure data,[27] contrary to the experimental findings.

This model has been pointed out to be fundamentally questionable for $3d^5$ ions in which the SO mechanism is important.[1] However, when the symmetry is slightly lower than cubic and the distortion is small, this model can reach an identical result to that of the microscopic mechanisms when treating the intrinsic parameter and the power-law exponent adjustability.[1] We have seen

TABLE IV. θ dependence of D in D_{3d} symmetry calculated by assuming $\bar{A}_2=5500$ cm^{-1} and $\bar{A}_4=600$ cm^{-1}, in units of 10^{-4} cm^{-1}.

θ (deg)	49	50	51	52	53	54	θ_c	55	56	57	58	59
D (SO-I)	−281	−248	−207	−159	−105	−46	0	16	80	143	205	262
D (SO-II)	−503	−400	−302	−212	−129	−52	0	18	79	132	178	212
D (accurate)[a]	−532	−422	−319	−223	−135	−54	0.04	18	83	139	187	224

[a] Calculated by $D=\frac{1}{6}[E(\pm\frac{5}{2})-E(\mp\frac{1}{2})]$.

that this model fails with crystal Fe^{3+}:Al_2O_3, which is strongly distorted.

V. CONCLUSION

The Γ_4 matrix of $D_3'(d^5)$ was derived, which is useful in calculating the axial splitting D. It is reasonable to omit the spin doublets in the calculation of this parameter. Both the SO-I and SO-II perturbation procedures are correct. However, the SO-I is usually applicable for weak distortion. The SO-II converges well in the trigonal case and can reach an excellent approximation when the sixth order is taken into account. In Fe^{3+}:Al_2O_3, the SO mechanism is the most important, and the rank-four field component plays a significant role in affecting the splitting. The CO mechanism contributes to D a negative value with a magnitude of 21% of the experimental value. All other mechanisms are two orders of magnitude smaller in contributing in this case.

---

[1] W. L. Yu and M. G. Zaho, Phys. Rev. B **37**, 9254 (1988).

[2] M. Blume and R. Orbach, Phys. Rev. **127**, 1587 (1962).

[3] R. R. Sharma, R. Orbach, and T. P. Das, Phys. Rev. **149**, 257 (1966).

[4] R. R. Sharma, Phys. Rev. B **3**, 76 (1971).

[5] H. Watanabe, Prog. Theor. Phys. **18**, 405 (1957).

[6] W. L. Yu, M. G. Zhao, and Z. Q. Lin, J. Phys. C **18**, 1857 (1985).

[7] J. Kondo, Prog. Theor. Phys. **23**, 106 (1960); **28**, 1026 (1962).

[8] R. R. Sharma, R. Orbach, and T. P. Das, Phys. Rev. **171**, 378 (1967).

[9] M. H. L. Pryce, Phys. Rev. **80**, 1107 (1950).

[10] R. Orbach, T. P. Das, and R. R. Sharma (unpublished).

[11] A. Van Heuveien, J. Chem. Phys. **46**, 4903 (1967).

[12] W. L. Yu and M. G. Zhao, J. Phys. C **17**, L525 (1984); **20**, 2931 (1987); **20**, 4647 (1987); Phys. Status Solidi B **140**, 203 (1987).

[13] Y. Y. Zhou, Phys. Status Solidi B **147**, 273 (1988); J. Phys. Condens. Matter **1**, 9911 (1989).

[14] G. G. Siu, J. Phys. C **21**, 3927 (1988).

[15] R. M. Macfarlane, J. Chem. Phys. **47**, 2066 (1967); Phys. Rev. B **1**, 989 (1970).

[16] K. Zdansky, Phys. Rev. **159**, 201 (1967).

[17] W. H. Baur and R. R. Sharma, J. Phys. C **19**, L229 (1986).

[18] W. L. Yu (unpublished).

[19] C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations* (MIT Press, Cambridge, MA, 1963).

[20] S. Febbraro, J. Phys. C **20**, 5367 (1987).

[21] S. Febbraro, J. Phys. C **21**, 2577 (1988).

[22] X. Y. Kuang, Phys. Rev. B **36**, 712 (1987).

[23] M. J. D. Powell, J. R. Gabriel, and D. F. Johnston, Phys. Rev. Lett. **4**, 410 (1960).

[24] M. L. Du and M. G. Zhao, J. Phys. C **18**, 3241 (1985).

[25] W. L. Yu, Phys. Rev. B **39**, 622 (1989).

[26] W. L. Yu, Phys. Rev. B **41**, 9415 (1990).

[27] R. E. Newnham and Y. M. De Haan, Z. Kristallogr. **117**, 235 (1962).

[28] D. J. Newman, Adv. Phys. **20**, 197 (1970).

[29] J. J. Krebs and W. J. Maisch, Phys. Rev. B **4**, 757 (1971).

[30] D. J. Newman, D. C. Pryce, and W. A. Runciman, Am. Mineral. **63**, 1278 (1978).

[31] A. Edgar, J. Phys. C **9**, 4304 (1976).

[32] S. Lee, C. M. Brodbeck, and C. C. Yang, Phys. Rev. B **15**, 2469 (1977).

[33] D. J. Newman and W. Urban, Adv. Phys. **24**, 793 (1975).

[34] D. J. Newman and E. Siegel, J. Phys. C **9**, 4285 (1976).