PHYSICAL REVIEW B VOLUME 55, NUMBER 14 1 APRIL 1997-II

g-factor formulas of $3d^5$ ions in trigonal-symmetry fields and their applications

M. G. Zhao and Y. Lei

Institute of Solid State Physics, Sichuan Normal University, Chengdu 610068, People's Republic of China

(Received 16 October 1996)

The g-factor formulas of $3d^5$ ions in C_{3v} symmetry are developed based on the equivalence between the phenomenological spin Hamiltonian and the microscopic Zeeman interaction. The formulas are universal ones and do not depend on the specific interaction model. Diagonalization of the complete Hamiltonian within the whole $3d^5$ configuration yields the theoretical zero-field splitting D, a, a-F, and g factors. The results for Mn^{2+} at the Li^+ site in $\mathrm{LiNbO_3}$ agree well with the experimental data. The Mn^{2+}(Li)-O^{2-} average bond length deduced ($R=2.0217$ Å) is comparable with those obtained from extended x-ray-absorption fine structure measurements, namely (2.06±0.05) Å. The d-d transition bands and EPR a value predicted can be verified by further experiments. [S0163-1829(97)03514-5]

I. INTRODUCTION

The microscopic calculation of g factors of $3d^5$ ions in crystals is much more difficult than that of other $3d^n$ ions. To our knowledge, there are no rigorous complete diagonalization calculation formulas on the g factors of $3d^5$ ions in a trigonal symmetry field. To understand the EPR characteristic of $3d^5$ ions in a $\mathrm{LiNbO_3}$ crystal, in this work we shall develop the microscopic calculation formulas on the g factors of $3d^5$ ions in crystals.

Lithium niobate ($\mathrm{LiNbO_3}$) is an important ferroelectric and nonlinear optical material for many technical applications (see, e.g., Refs. 1 and 2). Because of the similarity of the Li^+ and Nb^{5+} sites, one of the most difficult questions to answer with respect to defects in $\mathrm{LiNbO_3}$ is whether dopant ions substitute for Li^+ or Nb^{5+}. The decrease in the zero-field splitting (ZFS) parameter D with increasing temperature supports the conclusion that Mn^{2+} replaces Nb^{5+}.[3,4] This conclusion has also been reached on the basis of electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) studies.[5,6] An electron-nuclear double resonance (ENDOR) study favored Mn^{2+} at the Li^+ site.[7] This method can give direct information on the identity and the superhyperfine (SHF) and quadrupole interactions of the neighboring nuclei except those with zero nuclear spin (e.g., ^{16}O, the only abundant oxygen isotope). An extended x-ray-absorption fine structure (EXAFS) study also favored Mn^{2+} at the Li^+ site.[8] The comparison between the phases of Mn^{2+} in $\mathrm{LiNbO_3}$ and in aqueous solution yields a true $\mathrm{Mn}^{2+}(\mathrm{Li}^+)$-$\mathrm{O}^{2-}$ bond length of (2.06±0.05) Å.[8] Fluorescence spectra are rather noisy due to the low Mn concentration in their experiment and this limits the accuracy in the determination of atomic distances. However, their results clearly show that Mn^{2+} lies at the Li^+ site.

In this work, we apply both the complete diagonalization procedure (CDP) and an approximately equivalent self-consistent-field–molecular-orbital (SCF-MO) model[9,10] to determine the local structure of Mn^{2+} ions at Li^+ sites in $\mathrm{LiNbO_3}$. The result shows that the values calculated are in good agreement with the experimental findings.

II. MICROSCOPIC EXPRESSIONS FOR EPR PARAMETERS

By means of the approximate equivalence between the spin Hamiltonian (SH) method and the complete diagonalization procedure (CDP), the following microscopic expressions of ZFS parameters were obtained:[9]

$$D=(1/56)[(9\Delta_1/\sqrt{1+T^2})+\Delta_1-2\Delta_2], \tag{1}$$

$$a-F=(1/28)[(3\Delta_1/\sqrt{1+T^2})+18\Delta_2-9\Delta_1], \tag{2}$$

$$a=(3\Delta_1/\sqrt{80})(T/\sqrt{1+T^2}), \tag{3}$$

with

$$T=-2a_1a_2/(a_1^2-a_2^2), \tag{4}$$

$$\Delta_1=E(\Gamma_4+\pm 5/2)-E(\Gamma_4,\pm 1/2), \tag{5}$$

$$\Delta_2=E(\Gamma_6,\pm 3/2)-E(\Gamma_4,\pm 1/2), \tag{6}$$

where $E(\Gamma_4,\pm 5/2)$ and $E(\Gamma_4,\pm 1/2)$ denote the eigenenergies of Γ_4 (CDP) ground states of $|\pm 5/2\rangle$ and $|\pm 1/2\rangle$, respectively, and $E(\Gamma 6,\pm 3/2)$ is the eigenenergy of the Γ_6 (CDP) ground state of $|\pm 3/2\rangle$. a_1 and a_2 denote the CDP eigenvectors of the ground state of Γ_4,

$$|+1/2\rangle(\mathrm{CDP})=a_1|^6S,+1/2\rangle+a_2|^6S,-5/2\rangle \tag{7}$$

plus small contributions arising from $S=3/2$ and 1/2 states.

The theoretical calculation on g factors of $3d^5$ ions in crystals is much more difficult than that of other $3d^n$ ions. To our knowledge, there are no microscopic complete diagonalization calculation formulas on the g factors of $3d^5$ ions in a trigonal symmetry field.

By means of the approximate equivalence between the phenomenological SH and the microscopic Zeeman interaction, the following formulas are obtained:

TABLE I. d-d transitions and EPR parameters for $MnCO_3$ (all energies are in units of cm^{-1}).

Calculated (D_{3d} symmetry) Model parameters: $N=0.978\pm0.0001$ $q=(1.06\pm0.001)e$ Structure parameters: $R=(2.17\pm0.001)$ Å $\theta=(53.72\pm0.001)°$		Observed Ref. 18	 Ref. 16	 Ref. 15	 Ref. 17
$^6A_1(^6)$	0	0	0	0	0
$^4T_1(G)(^4A_2)$	18 521±20				
$^4T_1(G)(^4E)$	18 537±20	18 518	18 350	18 350	18 290
$^4T_2(G)(^4A_1)$	22 417±40	22 370	22 600	22 600	22 560
$^4T_2(G)(^4E)$	22 696±40	22 730			
$^4E(G)(^4E)$	24 490±15	24 510	24 510	24 580	24 500
$^4A_1(G)(^4A_1)$	24 495±15	24 750	24 540		24 740
$^4T_2(D)(^4E)$	27 770±40	27 400	27 620	27 255	27 330
$^4T_2(D)(^4A_1)$	27 935±40	27 700	27 950		27 580
$^4E(^4E)$	29 469±15	29 240	29 330	29 170	29 120
$^4T_1(P)(^4A_2)$	31 543±40	30 864	30 625	31 900	30 610
$^4T_1(P)(^4E)$	31 909±20	32 050	31 910		31 700
$^4A_2(F)(^4A_2)$	39 770±15				39 700
$^4T_1(F)(^4E)$	40 521±20			40 820	40 540
$^4T_1(F)(^4A_2)$	40 874±20				
$^4T_2(F)(^4E)$	43 301±20			41 670	
$^4T_2(F)(^4A_1)$	43 410±20				
EPR parameters		Observed (Refs. 19 and 20)			
$g_\parallel=2.0019\pm0.0005$ $g_\perp=2.0019\pm0.0005$		$g_\parallel=2.0018\pm0.0005$, $g_\perp=2.0013\pm0.0005$ $g=2.0019\pm0.0009$			
$D(10^{-4}\ cm^{-1})=-75.9\pm0.5$		$-75.7(\pm0.5)$, $\pm75(\pm0.5)$			
$(a\text{-}F)(10^{-4}\ cm^{-1})=6.27\pm0.5$		$7.35(\pm0.5)$			
$a(10^{-4}\ cm^{-1})=5.84\pm0.5$		$4.5(\pm0.5)$			

$$g_\parallel=g_{zz}=\frac{1}{3}\Bigg[\langle 5/2,3/2|\sum_{i=1}^{5}(kl_z(i)+2.0023S_z(i))|5/2,3/2\rangle - \langle 5/2,-3/2|\sum_{i=1}^{5}(kl_z(i) + 2.0023S_z(i))|5/2,-3/2\rangle\Bigg], \qquad (8)$$

$$g_\perp=g_{xx}=[(a_1^2+a_2^2)/2a_1^2]^{1/2}\langle 5/2,3/2|\sum_{i=1}^{5}(kl_x(i) + 2.0023S_x(i))|5/2,1/2\rangle,$$

where $(kL(i)+2.0023S(i))$ is the Zeeman magnetic moment operator of ith electron, k is the orbit reduction factor, and $|5/2,\pm3/2\rangle$ and $|5/2,\pm1/2\rangle$ denote the eigenfunctions of the ground state.

These expressions are universal ones and do not depend on the specific interaction model.

The matrices of both the Zeeman magnetic moment (dimension 252) and the complete Hamiltonian may be computer generated.[31]

III. VALIDITY OF TECHNIQUE

It is currently accepted that for impurities in solids the bond lengths, R_i, can be determined through the EXAFS technique. It may be applied to any kind of impurity. However, the impurity concentrations of the order 100 ppm may be difficult to see by EXAFS, while concentration of the order of 1 ppm of some transition-metal ions can be detected through EPR. Zhao *et al.*[9–11] show that the local structure of transition-metal ions in crystals can be determined from the optical and EPR spectra.

It must be pointed out that the local structure of impurity may differ from the host cation-anion one. In concentrated ruby, for instance, the Cr^{3+} ion has been found to be displaced from the host Al^{3+} ion site by 0.06 Å.[12]

Now, let us to study the validity of the technique for the determination of local structure through the optical and EPR spectra measurements.

Following the x-ray diffraction data,[13] the bond lengths and bond angles in $MnCO_3$ are as follows:

$$R=R_2=R_1=2.17\ \text{Å},$$

$$\theta=180°-\theta_2=\theta_1=53.7°. \tag{9}$$

The optical absorption spectra have been observed by some authors.[15–17]

In the approximately equivalent SCF-MO model,[9–11] the C_{3v} crystal-field parameters were given by

$$B_{20}=[-3eq\langle r^2\rangle/2]\sum_{i=1}^{2}(3\cos^2\theta_i-1)/R_i^3,$$

$$B_{40}=[-3eq\langle r^4\rangle/8]\sum_{i=1}^{2}(35\cos^4\theta_i-30\cos^2\theta_i+3)/R_i^5,$$

$$B_{43}=-B_{4-3}=[(\sqrt{35})3eq\langle r^4\rangle/4]\times[\sin^3\theta_2\cos\theta_2/R_2^5-\sin^3\theta_1\cos\theta_2/R_1^5]. \tag{10}$$

The crystal-field parameters, B_{kq}, can be calculated from the structure data provided that the expectation values $\langle r^n\rangle$ and the effective charge q are known. Considering the average covalency between central metal ion and ligand orbitals, a reasonable approximation was made that[9–11]

$$B=N^4B_0,\quad C=N^4C_0,\quad \alpha=N^4\alpha_0,\quad \beta=N^4\beta_0,$$

$$\zeta_d=N^2\zeta_d^0,\quad \langle r^n\rangle=N^2\langle r^n\rangle_0,\quad k=N^2, \tag{11}$$

where N measures the average reduction factor due to the covalency, and B_0, C_0, α_0, β_0, ζ_d^0, and $\langle r^n\rangle$, are the electrostatic parameters, Trees correction constant, Racah correction constant, the spin-orbit coupling constant, and the expectation value of r^n in the free ion state, respectively. As one sees, this model leaves at most two model parameters N and q, which remain to be determined from two theoretically or experimentally known energy levels. For the Mn^{2+} ion, we have[9]

TABLE II. d-d transitions and EPR parameters for $LiNbO_3{:}Mn^{2+}$ (all the energies are in units of cm^{-1}).

	Calculated (Li site, $f=0.939\pm0.001$)[a]		Calculated (Nb site, $f=0.973\pm0.001$)[b]	
O_h symmetry	C_{3v} symmetry		C'_{3v} symmetry	
$^6A_1(S)$ (ground state)	0.000 000 000		0.000 000 000	
	0.147 645 4264		0.150 999 4580	
	0.437 555 3337		0.435 823 0692	
$^4T_1(G)$	16 960	$^4A_2$	13 345	$^4A_2$
	16 980		13 426	
	17 767	^4E	13 806	^4E
	17 790		13 890	
	17 800		13 931	
	17 803		13 954	
$^4T_2(G)$	21 765	^4E	19 046	$^4A_1$
	21 876		19 059	
	21 912		19 146	^4E
	21 968		19 176	
	21 010	$^4A_1$	19 189	
	22 014		19 192	
$^4A_1(G)$ $^4E(G)$	24 474	$^4A_1$	24 407	$^4A_1$
	24 475		24 412	
	24 477	^4E	24 447	^4E
	24 487		24 464	
	24 495		24 485	
	24 501		24 492	
$^4T_2(D)$	27 195	$^4A_1$	26 914	$^4A_1$
	27 241		26 924	
	27 596	^4E	27 143	^4E
	27 694		27 233	
	27 748		27 273	
	27 800		27 418	

TABLE II. (*Continued.*)

Calculated (Li site, $f=0.939\pm0.001$)[a]			Calculated (Nb site, $f=0.973\pm0.001$)[b]	
O_h symmetry	C_{3v} symmetry		C'_{3v} symmetry	
$^4E(D)$	29 179 29 251 29 320 29 379	^4E	29 488 29 497 29 503 29 506	^4E
$^4T_1(P)$	31 703 31 784 31 893 32 040	^4E	34 068 34 179 34 260 34 370	^4E
	33 470 33 482	$^4A_2$	35 008 35 071	$^4A_2$
$^4A_2(F)$	39 731 39 863	$^4A_2$	39 834 39 837	$^4A_2$
$^4T_1(F)$	40 478 40 562	$^4A_2$	42 330 42 460	$^4A_2$
	41 378 41 403 41 511 41 540	^4E	42 509 42 722 42 793 42 850	^4E

EPR parameters		Observed (Refs. 5, 22, 23, and 24)
Li site	Nb site	
$g_\parallel=2.001\,887\pm0.0005$	$2.001\,686\pm0.0005$	$g=2.002\pm0.0005$
$g_\perp=2.001\,873\pm0.0005$	$2.001\,680\pm0.0005$	$g=1.995\pm0.005$
$\bar{g}=2.001\,88\pm0.0005$	$2.001\,683\pm0.0005$	$g=1.998\pm0.0025$
$D(10^{-4}\ \mathrm{cm}^{-1})=730\pm4$	724 ± 4	726 ± 6, 725, 725 ± 5
$(a\text{-}F)(10^{-4}\ \mathrm{cm}^{-1})=11.6\pm0.5$	36.7 ± 0.5	7.5 ± 4.5, 6 ± 6, 8 ± 5
$a(10^{-4}\ \mathrm{cm}^{-1})=6.6\pm0.5$	28.1 ± 0.5	

[a] $R_1^0=2.238$ Å, $R_2^0=2.068$ Å, $\theta_1=44.57°$, $\theta_2=110.26°$ (Refs. 10, 25–27).

[b] $R_1^0=1.889$ Å, $R_2^0=2.112$ Å, $\theta_1=61.65°$, $\theta_2=133°$ (Refs. 10, 25–27).

$$B_0=911\ \mathrm{cm}^{-1}\ (\text{observed, } 915\ \mathrm{cm}^{-1},\ \text{SCF, } 885\ \mathrm{cm}^{-1}),$$

$$C_0=3273\ \mathrm{cm}^{-1}$$

$$(\text{observed, } 3273\ \mathrm{cm}^{-1};\ \text{SCF, } 3059\ \mathrm{cm}^{-1}),$$

$$\zeta_d^0=336.6\ \mathrm{cm}^{-1}\ (\text{SCF, } 333\ \mathrm{cm}^{-1}),$$

$$\langle r^2\rangle=2.7755\ \text{a.u.},$$

$$\langle r^4\rangle=23.2594\ \text{a.u.} \tag{12}$$

Florez *et al.*[14] have performed the first Hartree-Fock-Roothaan calculation of the crystal-field spectrum of MnF_6^{4-} (isolated as well as inserted the RbMnF_3 lattice). Results show that first, the inclusion in the SCF calculation of the electrostatic potential due to the rest of the lattice does not modify the values of the optical transition energies, which supports the idea of cluster as good for understanding the properties of the transition-metal impurities in crystals, and second, the average covalency model is a good approximation since the SCF-MO transition energies can be described by the electrostatic parameters B and C, Trees correction constant α, Racah seniority correction-constant β, and the crystal-field parameter, which shows that the usual crystal-field theory is approximately equivalent to the SCF-MO model calculation. In the crystal-field-like model proposed by Zhao *et al.*,[9,10] the parameters B, C, α, β, ζ_d, B_{20}, B_{40}, and B_{43} were described by Eqs. (10)–(12) of this paper. By means of the approximate equivalence between the crystal-field model and the SCF-MO model, Zhao *et al.* have deduced the values of $N=0.98496$ and $q=e$ for MnF_6^{4-} cluster in RbMnF_3,[9] and the values of $N=0.9595$ and $q=2e$ for CrO_6^{9-} cluster in LiNbO_3.[10]

Since there are no SCF-MO calculation values of the optical transition energies for MnO_6^{10-} cluster in crystals, so the parameters N and q are determined from the optical absorption bands measurement, in the present work.

For Mn^{2+} ion in MnCO_3, we have deduced the values of $N=0.978\pm0.001$, $q=(1.06\pm0.001)e$ (Ref. 32), $R=(2.17\pm0.001)$ Å, and $\theta=53.72°\pm0.01°$ from the optical absorption bands.[15–18]

The result is listed in Table I. An excellent agreement between theoretical and experimental structure supports the determination of the local structure through the optical and EPR spectra. It means that the technique presented is correct.

IV. CALCULATION AND RESULTS FOR Mn^{2+} IN $\mathrm{LiNbO_3}$

As for $\mathrm{LiNbO_3{:}Mn^{2+}}$, no optical spectra have been published. However, we notice that the optical spectra of a lot of oxides containing Mn^{2+} ions are quite similar:[21] 16 500–19 000 cm^{-1} for ${}^4T_1(G)$, 21 000–23 000 cm^{-1} for ${}^4T_2(G)$, 23 000–24 800 cm^{-1} for ${}^4A_1(G)/{}^4E(G)$, 27 500–27 700 cm^{-1} for ${}^4T_2(D)$, and 28 600–29 300 cm^{-1} for ${}^4E(D)$. This enables us to estimate the model parameters N and q. Considering the structure similarity between $\mathrm{Mn}^{2+}-60^{2-}$ in $\mathrm{MnCO_3}$ and $\mathrm{Mn}^{2+}-60^{2-}$ in $\mathrm{LiNbO_3}$, $N=0.978$ and $q=1.06e$ are used in the calculation for $\mathrm{LiNbO_3{:}Mn^{2+}}$.

Considering the relaxation of the oxygen ligand, we define

$$f=R/R_0, \tag{13}$$

where R denotes the bond length of $\mathrm{Mn}^{2+}-60^{2-}$ in $\mathrm{Li^+/Nb^{5+}}$ site and R_0 is the bond length of $\mathrm{Li^+/Nb^{5+}}-60^{2-}$ in host $\mathrm{LiNbO_3}$.

For the Mn^{2+} ion in $\mathrm{LiNbO_3}$, we have deduced a value of $f=0.939$ from the EPR parameter D value.[5,22,26] The final results are listed in Table II. As one sees, an excellent agreement between theory and experiments is reached, as the Mn^{2+} ion substitutes for the Li^+ site. In contrast with this, the experimental EPR parameters cannot be reproduced placing the Mn^{2+} ion at Nb^{5+} position.

V. DISCUSSION AND CONCLUSION

(a) The microscopic g-factors calculation of $3d^5$ ions in crystal is much more difficult than that of other $3d^n$ ions. In this work the microscopic formulas on g factors of $3d^5$ ions in trigonal-symmetry field are developed based on the rigorous complete diagonalization procedure. These formulas are universal ones and do not depend on the specific interaction model. Applications show that the values calculated are in good agreement with experiments.

(b) We have deduced the values of $R=2.17$ Å and $\theta=53.72°$ from the EPR and optical absorption spectra of Mn^{2+} ions in $\mathrm{MnCO_3}$ which are in excellent agreement with the x-ray diffraction data,[13] which strongly supports that the local structure of Mn^{2+} ions in crystal can be determined through optical and EPR spectra. This is consistent with the conclusion reached in Refs. 9–11.

(c) We have deduced the values of $R_1=2.101\,482$ Å, $R_2=1.941\,852$ Å, and $R=2.021\,667$ Å for the $\mathrm{Mn^{2+}(Li){-}O^{2-}}$ bond lengths from the EPR D value (or, $f=0.939$). The average bond length deduced is comparable with those obtained from EXAFS measurement, namely (2.06 ± 0.005) Å.[8] The $g_\parallel$, $g_\perp$, and a-F values predicted are consistent with experiments within the range of experimental errors.

(d) The d-d transition bands and EPR a value predicted can be verified by further experiments.

(e) It must be pointed out that there is an error in the calculation by Yu and Zhao[28] because D (observed) is $(-199\pm7)\times10^{-4}$ cm^{-1} instead of $(34.5\pm5)\times10^{-4}$ cm^{-1} (see Ref. 29). Adopting the rigorous complete diagonalization procedure, the analytical expression for D value, and an approximately equivalent SCF-MO model,[9] we have deduced the bond lengths of $R_\parallel=2.09$ Å and $R_\perp=2.13$ Å for $\mathrm{MnF_2}$ from the experimental D value $(-199\pm7)\times10^{-4}$ cm^{-1} (Ref. 29) and the optical spectrum, which are consistent with the structure data by Baur[30] $[R_\parallel=(2.10\pm0.01)$ Å, $R_\perp=(2.13\pm0.027)$ Å$]$, which supports again the determination of the bond lengths through the optical and EPR measurements.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (Grant No. 19574036).

---

[1] A. Rauber, in *Current Topics in Material Science*, edited by E. Kaldis (North-Holland, Amsterdam, 1987), Vol. 1.

[2] F. F. Agullo-Lopez and J. M. Cabrera, *Properties of Lithium Niobate*, EMIS Datareview Ser. No. 5 (INSPEC, London, 1989).

[3] M. P. Petrov, Sov. Phys. Solid State **10**, 2574 (1969).

[4] G. I. Malovichko, A. A. Karmazin, I. P. Bykov, V. V. Laguta, and V. P. Yarunichev, Sov. Phys. Solid State **25**, 2038 (1983).

[5] T. Takeda, A. Watanabe, and K. Sugihara, Phys. Lett. **27A**, 114 (1968).

[6] S. H. Choh, H. T. Kim, H. K. Choh, C. S. Han, D. Choi, and J. N. Kim, Bull. Magn. Reson. **11**, 371 (1989).

[7] G. Gorradi, H. Sothe, J. M. Spaeth, and K. Polgar, J. Phys. Condens. Matter **2**, 6603 (1990).

[8] C. Zaldo and F. Agullo-Lopez, Solid State Commun. **71**, 243 (1989).

[9] M. G. Zhao and M. Chiu, Phys. Rev. B **52**, 10 043 (1995).

[10] M. G. Zhao and Y. Lei, J. Phys. Condens. Matter **9**, 529 (1997).

[11] M. G. Zhao, Phys. Status Solidi B **84**, 441 (1994).

[12] S. C. Moss and R. E. Newnham, Z. Kristallogr. **120**, 359 (1964).

[13] R. W. G. Wyekoff, *Crystal Structures* (Wiley-Interscience, New York, 1964), Vol. 2.

[14] M. Florez, L. Seijo, and Pueyo, Phys. Rev. B **34**, 1200 (1986).

[15] L. L. Lohr, J. Chem. Phys. **45**, 3611 (1966).

[16] A. L. P. Malecot, C. R. Acad. Sci. (Paris) **266**, 804 (1968).

[17] C. Y. Lin, H. B. Zhu, and Z. W. Ma, Acta Mineral. Sinica **1**, 40 (1981).

[18] F. Z. Lee, J. Sichuan Normal Univ. **3**, 44 (1984).

[19] G. E. Barberis, R. Calvo, H. G. Masdonado, and C. E. Zarate, Phys. Rev. B **12**, 853 (1975).

[20] F. K. Hurd, M. Sachs, and W. D. Herschberger, Phys. Rev. **93**, 3731 (1954).

[21] A. N. Platknow, *Meaning of Cloure of Minerals* (Science Press, Kiev, 1976) (Russian).

[22] J. B. Herrington, B. Dischler, and J. Schneider, Solid State Commun. **10**, 509 (1972).

[23] J. C. Danner, V. Ranon, and D. N. Stamires, Chem. Phys. Lett. **2**, 605 (1968).

[24] G. I. Malovichko, V. G. Grachev, and S. N. Lukin, Sov. Phys. Solid State **28**, 553 (1986).

[25] A. M. Glass, J. Chem. Phys. **50**, 1501 (1969).

[26] S. C. Abraham and P. Marsh, Acta Crystallogr. B **42**, 61 (1986).

[27] S. C. Abraham, W. C. Hamilton, and J. M. Reddy, J. Phys. Chem. Solids **27**, 1013 (1966).

[28] W. L. Yu and M. G. Zhao, J. Phys. C **18**, L1087 (1987).

[29] M. Tinkham, Proc. R. Soc. London Ser. A **236**, 535 (1956).

[30] V. W. Baur, Acta Crystallogr. **11**, 488 (1958).

[31] The matrices of both the energy and the magnetic moment of $3d^n$ ions ($n=1, 2, 3, 4, 5, 6, 7, 8, 9$) in C'_{3v} and C'_{2v} symmetry fields can be obtained from the authors.

[32] X. Y. Kuang (unpublished).