g-VALUE OF Fe^{3+} IN II–VI CUBIC CRYSTALS*

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Abstract—A theory of g-shift is developed of Fe^{3+} in II–VI cubic crystals. Electron-transfer through spin-orbit interaction to Fe^{3+} from the surrounding ligands is shown to be a reasonable mechanism for the observed positive g-shift in MgO, CaO, and ZnS.

1. INTRODUCTION

ELECTRON spin resonance of iron group S-state ions, for instance, Cr^+, Mn^{2+}, and Fe^{3+}, has been a subject of considerable interest in recent years. The g-values are very close to 2·0023, the free spin value. The small g-shift seems obvious since the approximate ground state, $3d^5\ ^6S$, has no orbital angular momentum. WATANABE[1] and later GABRIEL, JOHNSTON and POWELL[2] calculated the g-shift by the perturbation theory and obtained a definitely negative g-shift, no covalency being taken into account. The present author[3] found that a similar calculation based on partially covalent orbitals also led to a definitely negative g-shift. Positive g-shifts, however, have been reported on Fe^{3+} ion which replaces cations in cubic crystals, for instance, MgO,[4] CaO,[5] and ZnS.[6] FIDONE and STEVENS[7] suggest that there will be a contribution to the g-shift from electron transfer processes through spin-orbit interaction from the ligands to the S-state ion or the reverse transfer, and that the former transfer leads to a positive and the latter to a negative g-shift. The purpose of this work is to put the idea of electron transfer into a more detailed calculation for Fe^{3+} in II–VI cubic crystals, and to show that the g-shift calculated is favorably compared to the observed g-shifts of Fe^{3+} in MgO, CaO, and ZnS.

The host crystals just mentioned are assumed to be rather ionic; however, these should be partly covalent admixture between the 3d-orbitals of Fe^{3+} and the orbitals of the surrounding ligands. We shall take a paramagnetic complex consisting of the Fe^{3+} and the nearest ligands and take into account only ligand orbitals directed toward Fe^{3+}, i.e. σ-orbitals. The partially covalent orbitals are given in Appendix 1 for octahedral and tetrahedral complexes.

The approximate ground state of the paramagnetic complex is the totally symmetric state $^6A_1$.‡ The electron configuration of the state $^6A_1$ is such that the bonding orbital is completely filled, and the non-bonding and anti-bonding orbitals are partly filled with five electrons. Excited configurations associated with the transfer are the following: one hole is left in the bonding orbital, and six electrons are among the non-bonding and anti-bonding orbitals. The bonding-orbital is predominantly localized around the ligands; the non-bonding and anti-bonding orbitals around the central Fe^{3+} ion. The electron excitation from the bonding to the non-bonding or anti-bonding orbital may be interpreted as electron transfer from the ligands to the central ion.

The calculation of g-shift is reduced to the second-order perturbation calculation of energy correction for the ground state. The g-shift is

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‡ Mulliken's notation will be used for the irreducible representations of the cubic point group. The notation $^6A_1$ is used instead of ^6S since the single electron wavefunctions are linear combinations of d and σ-orbitals. Capital letters, A_1, A_2, E, T_1, and T_2, are used for many-electron operators and wave functions. Small letters, a_1, a_2, e, t_1, t_2, are used for single-electron operators and wavefunctions.

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given, for instance, by $\Delta g = (2/5)\Delta E/\beta H$, where β is Bohr magneton, H the applied magnetic field. ΔE is the second-order energy correction for the state $M_S = 5/2$, being linear both in the Zeeman Hamiltonian and the spin-orbit interaction.

In Section 2, calculation of g-shift is carried out on octahedral and tetrahedral complexes. Section 3 is devoted for qualitative discussions by comparing the observed g-shifts of Fe^{3+} in MgO, CaO, and ZnS to the theoretical formulas in this work.

2. SPIN-ORBIT TRANSFER

FIDONE and STEVENS[7] obtained an expression of the g-shift for an octahedral complex in the form

$$\Delta g = (2/5)(\zeta_a/\Delta E) \cdot |\langle xy|l_z|X^2 - Y^2 \rangle|^2$$

for the electron transfer from ligands to the S-state ion. The wavefunctions xy and $X^2 - Y^2$ used by Fidone and Stevens are explicitly given, in our case, by $t_2^n\zeta$ and $e^b v$ for the octahedral case in Appendix 1.* We shall further proceed the calculation for octahedral and tetrahedral complexes in the Sub-sections II-a and II-b.

(a) Octahedral complex

Many-electron wave functions may be written in terms of nine single-electron wave functions out of e^b, e^a, and t_2^n, others being omitted. The ground state $|^6A_1 M_S = 5/2\rangle$ is written in the single Slater determinant

$$|^6A_1, 5/2\rangle = [\xi\eta\zeta uv : u\bar{u}v\bar{v}] \qquad (1)$$

where letters on the left of colon are t_2^n and e^a orbitals and those on the right e^b orbitals. A letter with or without bar in it refers to a down- or up-spin state. There is only one configuration, $(t_2^n)^4(e^a)^2(e^b)^3$, which is connected by the spin-orbit interaction with the ground state $^6A_1$. This simply follows from the product representation: e (bonding orbital) $\times t_1$ (orbital part of the spin-orbit interaction) $= t_1 + t_2$. The configuration involves only one state $^6T_{1z}$ which has non-vanishing matrix elements of $\Sigma \zeta l_z \cdot s_z$ with the ground state $^6A_1$. The many-electron wavefunction for $|^6T_{1z}, M_S$

* The superscripts b, a and n, refer to "bonding", "anti-bonding" and "non-bonding" orbitals.

$= 5/2\rangle$ is also represented by the single determinant

$$|^6T_{1z}, 5/2\rangle = [\xi\eta\zeta\zeta uv : u\bar{u}v] \qquad (2)$$

The admixture of (2) into the ground state leads to the g-shift, which is calculated by second-order perturbation theory as

$$\Delta g = -(2/5) \cdot 2 \cdot \langle {}^6A_1, 5/2| \sum l_z | T_{1z} 5/2 \rangle$$

$$\times \langle {}^6T_{1z}, 5/2| \sum \zeta l_z s_z |{}^6A_1, 5/2\rangle/\Delta E$$

$$= -(4/5) \cdot (e^b\bar{v}|l_z|dt_z\zeta) \cdot \langle dt_2\zeta|\zeta(r)l_z s_z|e^b\bar{v}\rangle/\Delta E$$

$$\cong (8/5) \cdot \{(1 - \alpha^2) + \alpha(1 - \alpha^2)^{1/2}$$

$$\times \langle xev|dev\rangle\} \cdot \zeta_a/\Delta E \qquad (3)$$

where ΔE is the excitation energy from $^6A_1$ to $^6T_1$, and $\langle xev|dev\rangle$ is a group overlap integral. The calculation is actually carried out of Δg_z, which gives the isotropic g-shift. The approximation used is that the integral $\langle dev|\zeta(r)|xev\rangle$ is ignored since the function $\zeta(r)$ is approximately proportional to r^{-3} from origins and appreciable only at the vicinity of the origins. Matrix elements of orbital angular momentum operators with respect to dt_2 and de orbitals are given in Appendix II.

(b) Tetrahedral complex

For tetrahedral complexes, orbitals involved in the g-shift calculation are t_2^a, e^n and t_2^b. The ground state $|^6A_1, M_S = 5/2\rangle$ is

$$|^6A_1, 5/2\rangle = [\xi\eta\zeta uv : \xi\bar{\xi}\eta\bar{\eta}\zeta\bar{\zeta}]. \qquad (4)$$

The destination of transferred electron is the e^n or t_2^a orbital. This follows from the product: t_2 (bonding-orbital) $\times t_1$ (orbital part of the spin-orbit interaction) $= a_2 + e + t_1 + t_2$. Each of the two excited configurations $(t_2^a)^3 \cdot (e^n)^3 \cdot (t_2^b)^5$ and $(t_2^a)^4 \cdot (e^n)^2 \cdot (t_2^b)^5$, involves one $^6T_1$ state. The z-components with $M_S = 5/2$ are

$$|^6T_{1z}^n, 5/2\rangle = [\xi\eta\zeta uv\bar{v} : \xi\bar{\xi}\eta\bar{\eta}\zeta] \qquad (5)$$

and

$$|^6T_{1z}^a, 5/2\rangle = \frac{1}{\sqrt{2}}\{-[\xi\bar{\xi}\eta\zeta uv : \xi\bar{\xi}\eta\zeta\zeta]$$

$$-[\xi\eta\bar{\eta}\zeta uv : \xi\eta\bar{\eta}\zeta\zeta]. \qquad (6)$$

The superscripts, n and a, on T_1 refer to the electron destination. The g-shift due to the admixture

of these states is calculated as

$$\Delta g = -(4/5)[\langle t_2^b \zeta | l_z | e^n \bar{v} \rangle \cdot \langle e^n \bar{v} | \zeta(r) l_z s_z | t_2^b \zeta \rangle / \Delta E^n$$
$$+ \tfrac{1}{2} \{ \langle t_2^b \bar{\eta} | l_z | t_2^a \xi \rangle - \langle t_2^b \xi | l_z | t_2^a \bar{\eta} \rangle \}$$
$$\times \{ \langle t_2^a \xi | \zeta l_z s_z | t_2^b \bar{\eta} \rangle - \langle t_2^a \bar{\eta} | \zeta l_z s_z | t_2^b \xi \rangle \} / \Delta E^a]$$
$$\cong (8/5)[\{(1 - \alpha^2)$$
$$+ \alpha(1 - \alpha^2)^{1/2} \cdot \langle x t_2 \zeta | d t_2 \zeta \rangle \} \zeta_d / \Delta E^n \qquad (7)$$
$$+ \{ \alpha^2(1 - \alpha^2) + \alpha(1 - \alpha^2)^{1/2}(2\alpha^2 - 1)$$
$$\cdot \langle x t_2 \zeta | d t_2 \zeta \rangle \} \cdot \zeta_d / \Delta E^a].$$

Matrix elements, like $\langle x t_2 i | \zeta(r) | d t_2 i \rangle$, are neglected, i being ξ, η, ζ. Matrix elements, like $\langle \sigma_i | l_z | \sigma_j \rangle$ or $\langle \sigma_i | \zeta(r) l_z | \sigma_j \rangle$, are as small as or smaller than overlapping integrals between different ligands and are ignored, $i \neq j$ being names of ligands. $\langle \sigma_i | l_z | \sigma_i \rangle$ and $\langle \sigma_i | \zeta(r) l_z | \sigma_i \rangle$ are vanishing.

3. DISCUSSION OF THE COMPARISON WITH OBSERVED g-SHIFTS

The formulas, (3) and (7), involve four parameters: the spin-orbit, ζ_d; the ionicity, α^2; the group overlap integral; and the excitation energy, ΔE. No precise values are available for these parameters. Yet, one may be able to find their reasonable values as precise as the observed g-shifts and use formulas (3) and (7), to estimate the excitation energy for MgO, CaO and ZnS crystals. The excitation energies thus estimated are listed in the last column of Table 1, in which the observed g-shift and the parameters used are also listed. The parameters are tentatively evaluated as follows. The spin-orbit parameter, ζ_d, in a crystal is reduced to a smaller value than the free ionic value, 0·055 eV[8] although the interpretation is not clear yet.[9] The values of ζ_d are tentatively assumed, being about 0·8 times the free ionic value for MgO and CaO and about 0·8 and 0·6 times for ZnS. The value of ionicity, α^2, is taken from the article by TITLE.[6] Title's values are about 0·92 for MgO and CaO and 0·78 for ZnS. The difference, 0·02, between these and the values listed may be ignored compared to the experimental error in the g-shifts. The group overlap integrals are calculated with Slater radial functions. For MgO and CaO, the overlap is taken between $3de$ and the $2p$ σ-orbital of O^{--}. The σ-orbital is one of the tetrahedrally directed σ-orbitals constructed from $3s$ and $3p^3$. The formula (7) involves two excitation energies, ΔE^n and ΔE^a. The difference between these two energies may be well approximated by $10Dq$, i.e. the energy splitting between anti-bonding and non-bonding orbitals. PAPPALARDO and DIETZ[10] found that $10Dq$ for Mn^{3+} in CdS is about 7900 $cm^{-1} = 0·98$ eV. For the estimation of ΔE^n, the following approximation is made:

$$\Delta E^a \cong \Delta E^n + 10Dq \cong \Delta E^n + 1 \text{ eV}$$

The excitation energy should be less than the energy band gap, E_g, of the host crystal since the transferred electron is bound to the complex. The band gaps are 8·7 eV for MgO,[11] and 3·7 eV for ZnS.[12] The band gap for CaO is not found; however, one may safely predict it to be about

Table 1. *Observed g-shifts, parameters and estimated excitation energies*

Host crystal	Δg_{obs}	ζ_d (eV)	α^2	$\langle xev \| dev \rangle$ or $\langle xt_2 \zeta \| dt_2 \zeta \rangle$	Estimated ΔE^n (eV)
MgO	+0·0014[a] ±0·0007	0·045	0·9	0·241	8·7 ± 4·3
CaO	+0·0029[b] ±0·0005	0·045	0·9	0·154	3·6 ± 0·6
ZnS	+0·017[c] ±0·001	0·045 0·035	0·8	0·194	1·7 ± 0·1 1·3 ± 0·1

(a) Low W., *Phys. Rev.* **105**, 793 (1957).
(b) SHUSKUS A. J., *Phys. Rev.* **127**, 1529 (1962).
(c) TITLE R. S., *Phys. Rev.* **131**, 623 (1963).

Table 2. Symmetry classification of d-orbital and compatible linear combination of σ-orbitals for octahedral and tetrahedral complexes

d-orbital	Octahedral complex
deu	$xeu = (\frac{1}{12})^{1/2} \cdot (2\sigma_3 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_4 - \sigma_5)$
dev	$xev = (\frac{1}{2}) \cdot (\sigma_1 - \sigma_2 + \sigma_4 - \sigma_5)$
	Tetrahedral complex
$dt_2\xi$	$xt_2\xi = \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$
$dt_2\eta$	$xt_2\eta = \frac{1}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)$
$dt_2\zeta$	$xt_2\zeta = \frac{1}{2}(\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4).$

6 eV by extrapolation from the following series of crystals with the same structure as CaO:

CaS, 5·4 eV; CaSe, 5·0 eV; CaTe, 4·3 eV.

The excitation energies estimated appear to be of reasonable order of magnitude, although one cannot literally take these values because of the crudeness of the parameters used.

A means of examining the excitation energies estimated is suggested in the following. The Fe^{3+} resonance signal was observed in ZnS crystals under illumination of light, 365 mμ.[6] The mechanism may be interpreted as suggested by LAMBE, BAKER and KIKUCHI on CdS : Fe^{3+}.[13] The illumination excites an electron into the conduction band and leaves a hole in the valence band. The hole migrates in the crystal and is eventually trapped at Fe^{2+}. The electron is also trapped at some trap center. The process of hole trap may be such that the hole approaches to the paramagnetic complex around the Fe^{2+} and comes into the bonding orbital of the surrounding S^{--} ligands. The hole finally transfers into the non-bonding orbital, losing the energy ΔE^n. Similar arguments may be made on MgO and CaO. If the energy loss of hole could be observed, the measurement should be compared to the estimated excitation energies in this work.

4. CONCLUSION

A qualitative conclusion may be drawn that electron-transfer to Fe^{3+} from the surrounding ligands through the spin-orbit interaction gives rise to the positive g-shifts in II–VI cubic crystals.

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APPENDIX 1

Single electron wavefunctions used in the text are linear combinations of $3dt_2$, $3de$ orbitals and nearest ligand σ-orbitals of compatible symmetry. The σ-orbitals of compatible symmetry are listed with the corresponding σ-orbitals in Table A-1. For geometry and numbering of σ-orbitals, see the Fig. 1. The arrows indicate σ-orbitals directed toward the central ion. The x, y and z-axes are chosen along the principal axes of the regular polyhedron.
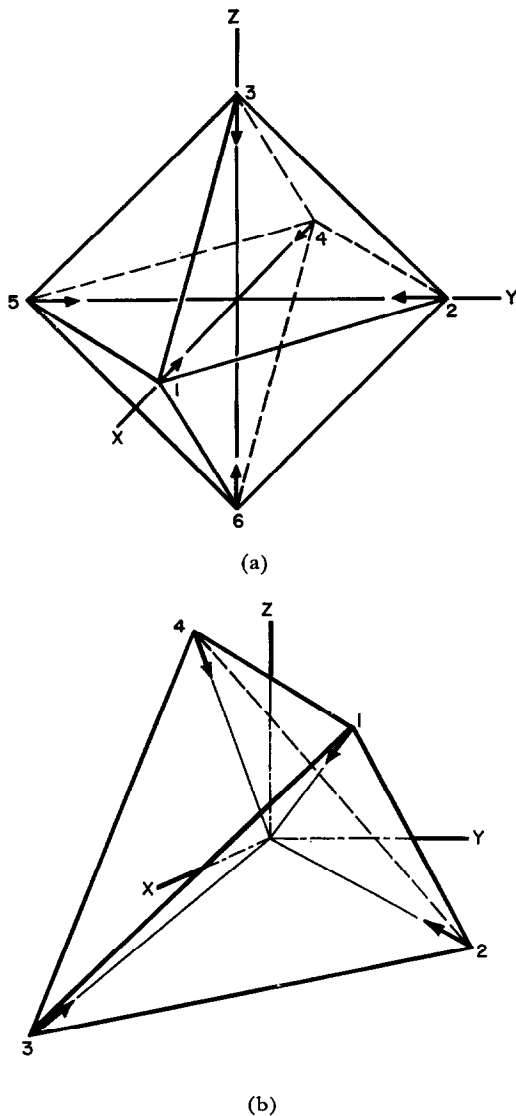
For an octahedral complex, the de and xe-orbitals are admixed and written in the form

$$|e^a, i\rangle = \alpha|de, i\rangle - (1-\alpha^2)^{1/2}|xe, i\rangle$$
$$|e^b, i\rangle = (1-\alpha^2)^{1/2}|de, i\rangle + \alpha|xe, i\rangle$$

where i refers to u and v components, and overlap integrals are neglected. For a tetrahedral complex, the antibonding and bonding-orbitals are written in the form

$$|t_2^a, i\rangle = \alpha|dt_2, i\rangle - (1-\alpha^2)^{1/2}|xt_2, i\rangle$$

and

$$|t_2^b, i\rangle = (1-\alpha^2)^{1/2}|dt_2, i\rangle + \alpha\cdot|xt_2, i\rangle$$

where

$$i = \xi, \eta \text{ and } \zeta.$$

APPENDIX 2

Matrix elements of orbital angular momentum operators, l_x, l_y, l_z, are given with respect to dt_2, ξ, η, ζ and deu, v orbitals.

$$\langle\xi|l_x|u\rangle = -\langle u|l_x|\xi\rangle = -i\sqrt{(3)}$$
$$\langle\xi|l_x|v\rangle = -\langle v|l_x|\xi\rangle = -\langle\eta|l_x|\zeta\rangle$$
$$= \langle\zeta|l_x|\eta\rangle = -i$$
$$\langle\xi|l_y|\zeta\rangle = -\langle\zeta|l_y|\xi\rangle = \langle\eta|l_y|v\rangle$$
$$= -\langle v|l_y|\eta\rangle = -i$$
$$\langle\eta|l_y|u\rangle = -\langle u|l_y|\eta\rangle = i\sqrt{(3)}$$
$$\langle\xi|l_z|\eta\rangle = -\langle\eta|l_z|\xi\rangle = i$$
$$\langle\zeta|l_z|v\rangle = -\langle v|l_z|\zeta\rangle = 2i$$

The dt_2, i and de, j orbitals are related to the orbital eigenfunctions $|l, m_e\rangle$, $l = 2$, $m_e = 2, \ldots, -2$ through

$$|dt_2, \xi\rangle = i(\tfrac{1}{2})^{1/2}\{|2, 1\rangle + |2, -1\rangle\}$$
$$|dt_2, \eta\rangle = (\tfrac{1}{2})^{1/2}\{-|2, 1\rangle + |2, -1\rangle\}$$
$$|dt_2, \zeta\rangle = i(\tfrac{1}{2})^{1/2}\{-|2, 2\rangle + |2, -2\rangle\}$$
$$|de, u\rangle = |2, 0\rangle$$
$$|de, v\rangle = (\tfrac{1}{2})^{1/2}\{|2, 2\rangle + |2, -2\rangle\}.$$

FIG. 1. Geometry and numbering of σ-orbitals for octahedral and tetrahedral coordinations. Arrows indicate σ-orbitals. (a) octahedron: The nearest ligands in rock-salt structure; (b) tetrahedron: The nearest ligand in zinc-blende structure.