

g Value of S -State Ions with $(ns)^1$ Configuration

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A theory of the g shift is developed of S -state ions with an outer-shell configuration $(ns)^1$ at octahedral and tetrahedral sites in crystals. A partial electron transfer through spin-orbit interaction from ligand ions to the S -state ion is assumed to be a dominant source for the g shift. A superhyperfine interaction is also calculated in terms of molecular-orbital parameters which are used in the g shift. Some experiments are suggested to confirm that the partial electron transfer is a dominant source for the g shift.

I. INTRODUCTION

RECENTLY, Sugibuchi observed the paramagnetic resonance spectra of Si^{3+} and Ge^{3+} ions which were incorporated into cubic ZnS crystals.¹ The g value is found to be 2.0047 for Si^{3+} and 2.0087 for Ge^{3+} , both being greater than the free-spin value 2.0023. The electronic configuration for these ions is $(ns)^1$ apart from the completely filled inner shells, where n is 3 for Si^{3+} and 4 for Ge^{3+} . The configuration leads to an electronic term 2S ; to a first approximation, the g value is the same as the free-spin value.

The purpose of this work is to develop a theory of g shift of S -state ions with the outer-shell configuration $(ns)^1$ at octahedral and tetrahedral sites in crystals, and to stimulate experiments which may determine if the theory is appropriate.

A few years ago the author developed a theory of the g shift of Fe^{3+} ions.² The theory qualitatively explains the observed g shift of Fe^{3+} ions.^{2,3} The theory assumes that a partial electron transfer through spin-orbit interaction from the ligand ions to Fe^{3+} ion is a reasonable source for the small, positive g shift. This mechanism was originally suggested by Fidone and Stevens.⁴

In Sec. II a theory of g shift for S -state ions with $(ns)^1$ is developed, assuming a mechanism similar to that assumed for Fe^{3+} in the previous work.² The ns electron has a vanishing orbital angular momentum, yet the observed g shift suggests that there must be some orbital contribution in addition to the spin magnetic moment. It will be shown that the partial electron transfer through the ligand spin-orbit interaction from the ligands to the S -state ion qualitatively explains the observed, positive g shift of S -state ions with $(ns)^1$. Theoretical expressions of the g shift involve atomic-orbital admixture coefficients in the molecular orbitals used. The admixture coefficients also appear in the superhyperfine (shf) constants. In Sec. III, relations are calculated between the admixture coefficients and the shf constants which may be determined from the

analysis of the shf spectra. Section IV discusses the theory and suggests some experiments.

II. CALCULATION OF g SHIFT

In the following calculations, the electron which shows the paramagnetic resonance is assumed to be confined within a cluster consisting of an S -state ion with $(ns)^1$ and the surrounding ligand ions. Effects of the rest of the host crystal are assumed to shift the energy levels of the cluster by a constant amount. The electron can actually move away outside of the cluster because of some perturbation arising from the rest of the host crystal; however, such a perturbation is ignored in the following calculations. Within the cluster, molecular orbitals concerned with the g shift are assumed to be linear combinations of the ns orbital of the S -state ion and the outer $n's$ and $n'p$ orbitals of the ligand ions. These assumptions are usually made to simplify calculations in the literature on the crystal field theory.⁵ In the following, the g shift is calculated for octahedral and tetrahedral clusters.

A. Octahedral Cluster SX_6

When a cluster is a regular octahedron as shown in Fig. 1, the point group that leaves the ionic configuration unaltered is the octahedral group O_h . The ns orbital of the S -state ion belongs to the identity representation of O_h , i.e., a_{1g} . The ns orbital may be admixed with linear combinations of the ligand $n's$ and $n'p$ orbitals through the electrostatic interaction between the electrons and also between the electrons and the

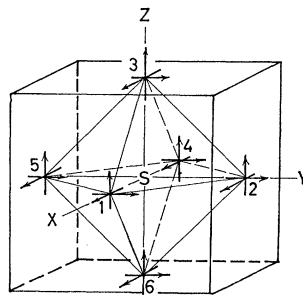


FIG. 1. Octahedral cluster SX_6 . Ligand $n'p$ orbitals are shown by arrows.

¹ K. Sugibuchi (private communication).

² H. Watanabe, J. Phys. Chem. Solids **25**, 1471 (1964).

³ K. Morigaki and T. Hoshina, Phys. Letters **17**, 85 (1965).

⁴ I. Fidone and K. W. H. Stevens, Proc. Phys. Soc. (London) **73**, 116 (1959).

⁵ For example, S. Sugano and R. G. Shulman, Phys. Rev. **130**, 517 (1963).

core charges within the cluster. Since the electrostatic interaction belongs to a_{1g} , the linear combinations that are admixed must also belong to a_{1g} . Such linear combinations are found to be

$$\chi_s = (\frac{1}{6})^{1/2} \{ (1s) + (2s) + (3s) + (4s) + (5s) + (6s) \}, \quad (2.1)$$

and

$$\chi_\sigma = (\frac{1}{6})^{1/2} \{ (1x) + (2y) + (3z) - (4x) - (5y) - (6z) \}, \quad (2.2)$$

where $(1s)$ is the $n's$ orbital of the ligand ion 1, and $(4x)$ is the $n'px$ orbital of the ligand ion 4. The geometry of the ligand $n'p$ orbitals is shown in Fig. 1. The anti-bonding molecular orbital of a_{1g} symmetry is expressed in a form

$$a_{1g} = N \{ \psi_s - \lambda_s \chi_s - \lambda_\sigma \chi_\sigma \}, \quad (2.3)$$

where ψ_s is the ns orbital of the S -state ion, and N is the normalization constant

$$N = (1 + \lambda_s^2 + \lambda_\sigma^2 - 2\lambda_s S_s - 2\lambda_\sigma S_\sigma)^{-1/2}. \quad (2.4)$$

S_s and S_σ are the group overlap integrals; all overlap integrals between different ligand ions are disregarded.

There are also molecular orbitals which do not admix with the ns orbital of the S -state ion. The molecular orbitals are classified by the symmetry properties as: $n's$ orbitals in e_g and t_{1u} ; $n'p\sigma$ orbitals in e_g and t_{1u} ; and $n'p\pi$ orbitals in t_{1g} , t_{2g} , t_{1u} , and t_{2u} . The orbital of $t_{1g}z$ symmetry is explicitly given by

$$t_{1g}z = \frac{1}{2} \{ (1y) - (2x) - (4y) + (5x) \}, \quad (2.5)$$

which will be used for the g -shift calculation.

A schematic illustration of energy levels for some of the molecular orbitals is shown in Fig. 2, where the relative position of the energy levels is not to scale. The levels for the molecular orbitals in the parentheses are not shown. The solid circles are the electrons in the ground state $|^2A_{1g}M_S = \frac{1}{2}\rangle$. In the following calculation, it is sufficient to take into account seven electrons in the antibonding a_{1g} and nonbonding t_{1g} orbitals. The wave function for the ground state is written in a single determinant

$$|^2A_{1g}M_S = \frac{1}{2}\rangle = [a_{1g} : x\bar{x}y\bar{y}z\bar{z}], \quad (2.6)$$

where a letter on the left of the colon is for the antibonding a_{1g} orbital, and those on the right are for the t_{1g} orbitals. A letter with or without a bar on it refers to a down- or up-spin state. The spin-orbit interaction of the ligand ions is treated as a perturbation which admixes excited states of T_{1g} symmetry into the ground state (2.6).⁶

When a magnetic field is applied along the Z direction, the octahedral cluster obtains the additional magnetic moment arising from the admixture of the wave function of $T_{1g}z$ symmetry, which is given by

$$|^2T_{1g}z M_S = \frac{1}{2}\rangle = [a_{1g} \bar{a}_{1g} : x\bar{x}y\bar{y}z\bar{z}]. \quad (2.7)$$

⁶ Capital letters, A_{1g} and T_{1g} , are used for many-electron states; small letters for single-electron states.

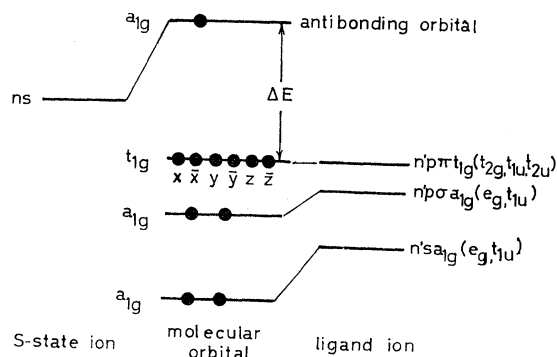


FIG. 2. Schematic illustration of energy levels for molecular orbitals in an octahedral cluster. Levels for the orbitals in the parentheses are not shown. The relative position of the levels is not to scale. Solid circles are the electrons in the ground state.

To find the g shift, the following expression should be calculated:

$$\Delta g_z = 2 \langle ^2A_{1g} | l_z | ^2T_{1g}z \rangle \langle ^2T_{1g}z | \zeta(r) l_z | ^2A_{1g} \rangle / \Delta E, \quad (2.8)$$

where $\zeta(r)$ is the spin-orbit interaction function of the $n'p$ electrons in the ligand ions, and ΔE is the energy separation between the antibonding a_{1g} and nonbonding t_{1g} orbitals as shown in Fig. 2. The magnetic quantum number M_S is omitted in (2.8) since the spin part of the matrix elements need not be calculated. The g shift calculated with the use of (2.3) and (2.5) is

$$\Delta g = (\frac{2}{3}) N^2 \{ \lambda_\sigma^2 - i \lambda_\sigma \lambda_s R \hbar^{-1} \langle 1y | p_y | 1s \rangle \} \zeta / \Delta E, \quad (2.9)$$

where R is the distance between the S -state ion and one of the ligand ions, and $\langle 1y | p_y | 1s \rangle$ is an off-diagonal matrix element of the y component of the linear momentum. A subscript z is omitted in (2.9) since $\Delta g_x = \Delta g_y = \Delta g_z$ because of the symmetry of the cluster. Equation (2.9) is further rewritten as

$$\Delta g = (\frac{2}{3}) N^2 \{ \lambda_\sigma^2 + \lambda_\sigma \lambda_s m R \times \langle n'px | x | n's \rangle \Delta E(p-s) / \hbar^2 \} \zeta / \Delta E, \quad (2.10)$$

where m is the electronic mass, and $\Delta E(p-s)$ is the energy separation between the $n'p$ and $n's$ orbitals. In calculating (2.10), two relations $dy/dt = (i\hbar)^{-1} (y\mathbf{H} - \mathbf{H}y)$ and $\langle n'py | y | n's \rangle = \langle n'px | x | n's \rangle$ are used, where \mathbf{H} is the Hamiltonian operator for the ligand ion.

It may be noted that the admixture of (2.7) into (2.6) is qualitatively interpreted as a partial electron-transfer from the ligand ions to the S -state ion. The molecular orbital t_{1g} is localized on the ligand ions, and the antibonding orbital a_{1g} is mainly localized on the S -state ion. The partial electron transfer leads to the g shift (2.10) of the S -state ion in the octahedral cluster when the cluster is subjected to an applied magnetic field.

B. Tetrahedral Cluster SX_4

A tetrahedral cluster is illustrated in Fig. 3. The Cartesian axes for each ligand ion are chosen so that

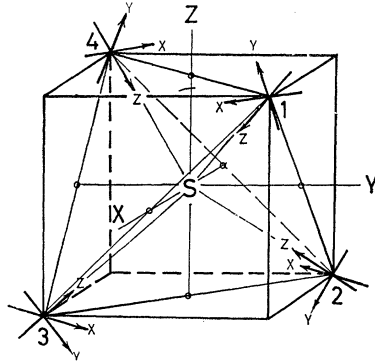


FIG. 3. Tetrahedral cluster SX_4 . Ligand $n'p$ orbitals are shown by arrows.

each z axis is directed toward the central S -state ion. More specifically, the direction cosines of the $1x$, $1y$, and $1z$ axes for the ligand ion 1 with respect to the X , Y , and Z axes are as listed in Table I. Those for other ligand ions are obtained by rotating the axes of the ligand ion 1 around the central S -state ion into the other ligand ions. The point group of the tetrahedral cluster is the tetrahedral group T_d . The ns orbital of the S -state ion belongs to the identity representation of T_d , i.e., a_1 . Linear combinations of the $n's$ orbitals of the ligand ions are also classified in a_1 and t_2 ; those of the $n'pz$ orbitals in e , t_1 , and t_2 . Molecular orbitals concerned with the g -shift calculation are

$$a_1 = N\{\psi_s - \lambda_s \chi_s - \lambda_\sigma \chi_\sigma\}, \quad (2.11)$$

and

$$t_1 z = \frac{1}{2}\{(1x) - (2x) - (3x) + (4x)\}, \quad (2.12)$$

where

$$\chi_s = \frac{1}{2}\{(1s) + (2s) + (3s) + (4s)\}, \quad (2.13)$$

and

$$\chi_\sigma = \frac{1}{2}\{(1z) + (2z) + (3z) + (4z)\}. \quad (2.14)$$

A schematic pattern of the energy levels for some of the molecular orbitals is illustrated in Fig. 4, where the levels for the molecular orbitals in the parentheses are not shown.

Seven electrons in the antibonding a_1 and non-

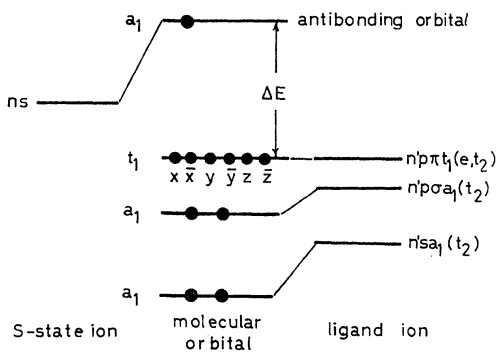


FIG. 4. Schematic illustration of energy levels for molecular orbitals in a tetrahedral cluster. Levels for the orbitals in the parentheses are not shown. The relative position of the levels is not to scale. Solid circles are the electrons in the ground state.

bonding t_1 orbitals are taken into account. The wave function for the ground state $|^2A_1M_S=\frac{1}{2}\rangle$ is written in the single determinant

$$|^2A_1M_S=\frac{1}{2}\rangle = [a_1 : x\bar{x}y\bar{y}z\bar{z}]. \quad (2.15)$$

When a magnetic field is applied along the Z axis, the calculation of the g shift is carried out in the same manner as the case A . It is found that

$$\Delta g = \left(\frac{4}{3}\right)N^2\{\lambda_\sigma^2 - i\lambda_\sigma\lambda_s R\hbar^{-1}\langle 1x | p_x | 1s \rangle\} \zeta / \Delta E, \quad (2.16)$$

where R is the distance between the S -state ion and one of the ligand ions. Equation (2.16) is rewritten as

$$\Delta g = \left(\frac{4}{3}\right)N^2\{\lambda_\sigma^2 + \lambda_\sigma\lambda_s mR \times \langle n'pz | x | n's \rangle \Delta E(p-s) / \hbar^2\} \zeta / \Delta E. \quad (2.17)$$

It is to be noted that (2.10) and (2.17) are identical, and that the magnitudes of the parameters involved depend on the S -state ion, the ligand ions, and the configuration of the cluster. The magnitudes of $N\lambda_\sigma$ and $N\lambda_s$ in (2.10) and (2.17) may be estimated from the shf measurements. In the next section expressions for the shf constants are calculated in terms of $N\lambda_\sigma$ and $N\lambda_s$.

TABLE I. The direction cosines of $1x$, $1y$, and $1z$ for the ligand 1 with respect to the X , Y , and Z axes as shown in Fig. 3.

	X	Y	Z
$1x$	$(\frac{1}{2})^{1/2}$	$-(\frac{1}{2})^{1/2}$	0
$1y$	$-(\frac{1}{6})^{1/2}$	$-(\frac{1}{6})^{1/2}$	$2(\frac{1}{6})^{1/2}$
$1z$	$-(\frac{1}{3})^{1/2}$	$-(\frac{1}{3})^{1/2}$	$-(\frac{1}{3})^{1/2}$

III. CALCULATION OF shf CONSTANTS

The unpaired electrons within the cluster interact with the nuclear magnetic moment of the ligand ions. The magnetic dipolar interaction is

$$\sum_j g\beta g_j \beta_n r_j^{-3} \{3(\mathbf{s} \cdot \mathbf{r}_j)(\mathbf{I}_j \cdot \mathbf{r}_j) r_j^{-2} - (\mathbf{s} \cdot \mathbf{I}_j)\}, \quad (3.1)$$

where the summation is to be taken over the ligand nuclei; g_j is the nuclear magneton number of the nucleus j ; β_n is the nuclear magneton; \mathbf{I}_j is the nuclear spin; and \mathbf{r}_j is the vector connecting the electron and the nucleus j . The expected value of (3.1) may be immediately calculated with respect to the orbital part of the ground state, (2.6) of (2.15).⁷ The result is

$$\sum_j \{A_{js} \mathbf{s} \cdot \mathbf{I}_j + (A_{ja} + A_{j\sigma})(3s_z I_{jz} \cos^2\theta_j - \mathbf{s} \cdot \mathbf{I}_j)\}, \quad (3.2)$$

where

$$\begin{aligned} A_{js} &= g\beta g_j \beta_n (8\pi/3) |\psi_{n's}(0)|^2 f(N\lambda_s)^2 \\ &= A_{js}^0 f(N\lambda_s)^2, \end{aligned} \quad (3.3)$$

$$\begin{aligned} A_{j\sigma} &= g\beta g_j \beta_n \langle r^{-3} \rangle_{n'p} f_{\frac{2}{3}}^2 (N\lambda_\sigma)^2 \\ &= A_{jp}^0 f_{\frac{2}{3}}^2 (N\lambda_\sigma)^2, \end{aligned} \quad (3.4)$$

⁷ For example, H. Watanabe, *Operator Methods in Ligand Field Theory* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1966), Chap. 4, p. 139.

and

$$A_{js^0} = g\beta g_j \beta_n R^{-3} N^2. \quad (3.5)$$

A_{js^0} and A_{jp^0} are the hyperfine (hf) constants for the ligand ion j in the free-ionic state. The numerical factor f is $\frac{1}{6}$ for the octahedral cluster and $\frac{1}{4}$ for the tetrahedral cluster. θ_j is the angle between the applied magnetic field and the axis connecting the S -state ion and the ligand ion j . The subscript ζ indicates the direction of the applied magnetic field. In calculating (3.3) and (3.4), all integrals involving the orbitals of two ligand ions are ignored; the integral over the ns orbital of the S -state ion in (3.5) is replaced by a point dipole located at the S -state ion. The magnitudes of $N\lambda_s$ and $N\lambda_\sigma$ may be known by comparing the shf constants with the corresponding hf constants of the free ions.

IV. DISCUSSION

As is mentioned in the Introduction, experiments on Si^{3+} and Ge^{3+} ions were made by Sugibuchi, who found a small, positive g shift in cubic ZnS crystals.¹ The g shift (2.17) applies here and shows that the partial electron transfer through the spin-orbit interaction in the ligand ions leads to the positive g -shift. Sugibuchi's observation may be a piece of evidence confirming the partial electron transfer as being a reasonable source for the observed g shift.

The g shifts (2.10) and (2.17) are proportional to the spin-orbit constant ζ , the magnitude of which differs with the species of the ligand ions. Examples of the ligand ions are a series of F^- , Cl^- , Br^- , and I^- , and a series of O^{--} , S^{--} , Se^{--} , and Te^{--} . Though the magnitudes of ζ for these negative ions are not known, the ratios of ζ may be close to those for the neutral atoms. The magnitudes and ratios for the latter are listed in Table II. It is expected that the g shift increases, for example, if S^{--} ions are replaced by Se^{--} ions, since other quantities in (2.10) and (2.17) do not vary from S^{--} to Se^{--} as does ζ . It is interesting to perform such experiments to see if this is actually the case.

As suggested at the end of Sec. II, the admixing parameters $N\lambda_s$ and $N\lambda_\sigma$ may be estimated using (3.3) and (3.4) from the measurements of the shf constants. For this, observation of shf structure is proposed using host crystals with ligand ions possessing a nuclear moment. It is to be noted that the magnitudes of hf constants, A_{js^0} and A_{jp^0} , are known for F^- ,⁸ Cl^- , and Br^- ,⁹ but are not known for other ions listed in Table II.

The magnitudes of the quantity $\langle n'p_x|x|n's \rangle \times \Delta E(p-s)/\hbar^2$, for F^- , Cl^- , and Br^- may be roughly estimated using the self-consistent calculations from

⁸ R. G. Shulman and S. Sugano, Phys. Rev. **130**, 506 (1963).

⁹ W. Hayes, J. R. Pilbrow, and L. M. Slifkin, J. Phys. Chem. Solids **25**, 1417 (1964).

TABLE II. Magnitudes and ratios of spin-orbit constants ζ for neutral atoms. Wave number units (cm^{-1}) are used.

	F	Cl	Br	I	O	S	Se	Te
ζ	296 ^a	587 ^a	2456 ^b	5069 ^c	136-158 ^a	352-396 ^a	1868 ^d	4203 ^e
Ratio	1	2.0	8.3	17	1-1.2	2.6-2.9	13.7	30.9

^a C. E. Moore, Natl. Bur. Std. (U.S.) Circ. 467 (1949).

^b C. E. Moore, Natl. Bur. Std. (U.S.) Circ. 467 (1952).

^c C. E. Moore, Natl. Bur. Std. (U.S.) Circ. 467 (1958).

^d Referred to in M. Blume and R. E. Watson, Proc. Roy. Soc. (London) **A271**, 565 (1963).

^e E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1953), 2nd ed.

first principles,¹⁰ while those for other ions listed in Table II may be compared with those for the neutral atoms multiplied by some reduction factor.

In a first approximation, the level for the nonbonding t_{1g} in the octahedral cluster (t_1 in the tetrahedral cluster) is located in the same energy as the levels for the nonbonding $n'p\sigma t_{1u}$ and $n'p\pi t_{1u}$ ($n'p\sigma t_2$ and $n'p\pi t_2$). If the host crystal is irradiated with light in the energy region including the energy difference ΔE involved in (2.10) [(2.17)], an electron in the latter orbitals will be excited into the antibonding orbital $a_{1g}(a_1)$. Under the illumination, some of the clusters in the host crystal get in a state whose g value differs from that before the electronic excitation. Thus the intensity of the paramagnetic resonance spectra should be reduced by the illumination. Sugibuchi has observed such an intensity reduction on Si^{3+} and Ge^{3+} in ZnS crystals in his preliminary experiments.¹

In calculating the g shifts [(2.10) and (2.17)] the cluster around the S -state ion under consideration is assumed to be placed in a constant potential arising from the rest of the host crystal. The unpaired electron within the cluster is assumed not to go out of the cluster; the electrons in the rest of the host crystal are also assumed not to come into the cluster. These assumptions should be carefully examined when the host crystal is irradiated with light. It may be possible that an electron outside the cluster is excited by the illumination and is trapped in the cluster. The intensity of the paramagnetic resonance spectra may also be reduced by such a process. The photon energy that corresponds to the energy difference ΔE must be carefully identified.

In conclusion, attention is called to the value of making paramagnetic resonance experiments on S -state ions with $(ns)^1$ in varied crystals under illumination.

ACKNOWLEDGMENT

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¹⁰ For F^- , C. Froese, Proc. Cambridge Phil. Soc. **53**, 206 (1963); for Cl^- and Br^- , D. F. Mayers, unpublished calculations referred to in Ref. 9.