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Spin-spin interaction in $f^7({}^8S)$-state ions in solids: Evaluation of the zero-field splitting of Gd^{3+} ion in lanthanum ethyl sulfate

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The spin-spin interaction between electrons has been taken into account to derive for the first time explicit expressions for the zero-field-splitting parameter of an $f^7({}^8S)$-state ion in axial crystalline fields considering all the allowed electronic distortions. By evaluating the derived expressions for Gd^{3+} in lanthanum ethyl sulfate it has been demonstrated that the spin-spin mechanism is indeed very important and should not be neglected.

The importance of the spin-spin interaction for an S-state $3d$ transition-metal ion was first pointed out by Pryce,[1] who allowed the distortion of the ground state of the ion by the electronic dipole-dipole interaction and obtained a nonvanishing value of the matrix element of the axial (or rhombic) crystalline fields. Pryce took into account only the excitation between the ground state $3d^5({}^6S)$ and the excited state ${}^6D(3d^44s)$ of the ion. Subsequently, this mechanism was further extended by Chakravarty,[2] and Sharma, Das, and Orbach,[3] for $3d^5({}^6S)$ ions by taking not only all the allowed s-like, but also the allowed d- and g-like, admixtures into the ground-state wave functions via spin-spin interaction. The expressions derived in Ref. 3 for the s-, d-, and g-like excitations have been found to be very useful and have been employed by various researchers[4–13] to estimate the important contribution from the spin-spin mechanism to the zero-field splittings of Mn^{2+} and Fe^{3+} ions in different crystalline environments.

As for the $4f^7({}^8S)$ rare-earth ions, the Pryce mechanism has been discussed by Wybourne,[14] who expressed the zero-field splitting as arising from the excitation from the ground state to the excited state $|4f^6({}^7F)6p\,{}^8D_{7/2}\rangle$,

$$D_p \propto \langle 4f^7\,{}^8S_{7/2}M' \,|\, H_{\text{ss}} \,|\, 4f^6({}^7F)6p\,{}^8D_{7/2}M\rangle \times \langle 4f^6({}^7F)6p\,{}^8D_{7/2}M \,|\, V_{\text{ax}} \,|\, 4f^7\,{}^8S_{7/2}M'\rangle \qquad (1)$$

where H_{ss} is the spin-spin interaction given by

$$H_{\text{ss}} = g^2\beta^2 \sum_{i<j} \left[\frac{(\vec{s}_i \cdot \vec{s}_j)}{r_{ij}^3} - \frac{3(\vec{s}_i \cdot \vec{r}_{ij})(\vec{s}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right] ,$$

and V_{ax} is the axial crystalline field.

Wybourne was unable to make a realistic evaluation of the splitting from Eq. (1) because the relevant Marvin integrals were not available. However, he inferred that the spin-spin mechanism by itself cannot explain the observed zero-field splitting of Gd^{3+} in crystals, particularly in lanthanum ethyl sulfate. Since then, this mechanism appears to have been consistently discarded in the literature in the further analysis of the experimental data of $f^7({}^8S)$-state ions.

It is evident from the above that neither the spin-spin interaction alone, nor a crystal field alone, can remove the degeneracies of the S-state ions. In fact, only the simultaneous action of the crystal fields and interactions such as spin-spin or spin-orbit interactions in high orders is necessary to split the S state. In addition to the spin-spin mechanism, Wybourne has considered seven more splitting mechanisms: (1) a fourth-order mechanism that is cubic in spin-orbit interaction but linear in the crystal-field strength, (2) a fourth-order mechanism with second-order effects of crystal fields and spin-orbit interaction, (3) a third-order spin-spin mechanism within the $4f^7$ configuration, (4) a second-order mechanism considering the relativistic nature of the wave function with linear effects of spin-orbit interaction and the crystal-field strength, (5) a crystal-field configuration-mixing mechanism involving second-order effects of the crystal fields and the excited configurations, (6) a correlation crystal-field mechanism which effectively modifies the Coulomb interaction between the open-shell electrons because of the crystalline environment, and (7) a fifth-order configuration-interaction mechanism quadratic in spin-orbit interaction, quadratic in Coulomb potential, and linear in crystal fields. For details of the calculations from these mechanisms, see Ref. 14.

As is clear and has been pointed out in Ref. 13, Eq. (1) gives only a part of the contribution arising from $f \rightarrow p$ type excitations and, analogous to the contributions from $d \rightarrow s$, $d \rightarrow d$, and $d \rightarrow g$ excitations for the iron-group ions, we would expect, in addition, contributions from $f \rightarrow f$ and $f \rightarrow h$ excitations appropriate to the rare-earth ions. However, such contributions have not yet been obtained, probably due to the complexity involved in the evaluation of the nondiagonal matrix elements of H_{ss}. The aim of this work is to present a complete and explicit evaluation of the zero-field splitting of $f^7({}^8S)$ ions arising from all types of allowed excitations via the spin-spin interaction in an axial crystalline field, and to revive the spin-spin mechanism for the future analysis of the experimental data. Our present calculations of the spin-spin contribution to the splitting for Gd^{3+} in lanthanum ethyl sulfate reveal that the spin-spin contribution is indeed very significant and should not be neglected.

First, we present our procedure for deriving the expressions for D, the zero-field splitting parameter, in the spin Hamiltonian

$$H_S = D[3S_Z^2 - S(S+1)] \ , \tag{2}$$

due to the spin-spin interaction for the $f^7(^8S)$ state in an axial potential of order k, i.e., V_k^0 (with the notation[3] for crystal potential $V_{\text{cryst}} = \sum_{k,m_k} V_k^{m_k}$ where $m_k = 0$ gives the axial part),

$$V_k^0 = -p_k^0 \sum_i r_i^k Y_k^0(\theta_i, \phi_i) \ , \tag{3}$$

where r_i, θ_i, and ϕ_i are the spherical coordinates for the ith electron on the rare-earth ion, and p_k^0 is a constant which defines the required axial crystal field. We recall that only the axial crystal fields are expected to contribute to D.

According to our procedure, we construct the $f^7(^8S)$ ground-state determinant out of the perturbed one-electron f orbitals due to the perturbation V_k^0. The matrix elements of the spin-spin interaction H_{ss} between the perturbed $|\, S, M_S \rangle$ ground-state levels are then

$$X_{\text{ss}}(M_s', M_s) = {}' \langle {}^8S, M_S' \,|\, H_{\text{ss}} \,|\, {}^8S, M_s \rangle' \ . \tag{4}$$

The "prime" on the wave functions in Eq. (4) signifies that the one-electron states used in constructing the multielectron ground-state determinant are perturbed by V_k^0. Accordingly,

$$|\, {}^8S, M_s \rangle' = \sqrt{1/7!}\, \epsilon_{\alpha,\beta,\gamma,\delta,\epsilon,\theta,\xi} \psi_\alpha^{(1)}(1) \psi_\beta^{(1)}(2) \psi_\gamma^{(1)}(3) \psi_\delta^{(1)}(4) \psi_\epsilon^{(1)}(5) \psi_\theta^{(1)}(6) \psi_\xi^{(1)}(7) \ , \tag{5}$$

$$|\, {}^8S, M_S \rangle = \sqrt{1/7!}\, \epsilon_{\alpha,\beta,\gamma,\delta,\epsilon,\theta,\xi} \psi_\alpha^{(0)}(1) \psi_\beta^{(0)}(2) \psi_\gamma^{(0)}(3) \psi_\delta^{(0)}(4) \psi_\epsilon^{(0)}(5) \psi_\theta^{(0)}(6) \psi_\xi^{(0)}(7) \ . \tag{6}$$

In Eq. (5), $\psi_m^{(1)}(i)$ constitutes the perturbed one-electron f orbitals such that

$$\psi_m^{(1)}(i) = \psi_m^{(0)}(i) + \delta\psi_m(i) \ , \tag{7}$$

where $\delta\psi_m(i)$ is the first-order perturbation on the unperturbed one-electron f orbitals $\psi_m^{(0)}(i)$ with $m = \pm 3, \pm 2, \pm 1, 0$, which is determined by solving the following differential equations from the quantum-mechanical first-order perturbation theory. We have

$$(H_i^0 - \epsilon_i^0)\delta\psi(i) = -h_1 \psi^{(0)}(i) + \sum_j \langle \psi^{(0)}(j) \,|\, h_1 \,|\, \psi^{(0)}(i) \rangle \psi^{(0)}(j) \ , \tag{8}$$

with $h_1 = -p_k^0 r^k Y_k^0$. The spin-spin contribution to D is then given by

$$D_{\text{ss}} = \tfrac{1}{18}[X_{\text{ss}}(\tfrac{7}{2}, \tfrac{7}{2}) - X_{\text{ss}}(\tfrac{5}{2}, \tfrac{5}{2})] \ ,$$

which upon evaluation of the spin-dependent matrix elements becomes,

$$D_{\text{ss}} = -\frac{1}{42} \frac{g^2\beta^2}{a_0^3} \left\langle {}^8S \left| \sum_{i<j} \frac{(3z_{ij}^2 - r_{ij}^2)}{r_{ij}^5} \right| {}^8S \right\rangle' \ . \tag{9}$$

After the detailed and tedious algebraic simplification for the evaluation of the matrix element in Eq. (9), one obtains, for $k = 4$ and 6,

$$D_{\text{ss}} = 0 \ ,$$

and, for $k = 2$,

$$D_{\text{ss}} = D_{\text{ss}}(f \to p) + D_{\text{ss}}(f \to f) + D_{\text{ss}}(f \to h) \ , \tag{10}$$

where

$$D_{\text{ss}}(f \to p) = -\frac{g^2\beta^2}{42a_0^3} \frac{\sqrt{5}}{\sqrt{4\pi}} p_2^0 [\tfrac{108}{25} h_{f\to p}^{0,3} - \tfrac{36}{25} g_{f\to p}^{2,5} - \tfrac{8}{25} h_{f\to p}^{2,5} - 8 g_{f\to p}^{4,7}] \ , \tag{11}$$

$$D_{\text{ss}}(f \to f) = -\frac{g^2\beta^2}{42a_0^3} \frac{\sqrt{5}}{\sqrt{4\pi}} p_2^0 [-\tfrac{56}{75} g_{f\to f}^{0,3} + \tfrac{112}{25} h_{f\to f}^{0,3} - \tfrac{112}{75}(g_{f\to f}^{2,5} + h_{f\to f}^{2,5}) - \tfrac{56}{33}(g_{f\to f}^{4,7} + h_{f\to f}^{4,7})] \ , \tag{12}$$

$$D_{\text{ss}}(f \to h) = -\frac{g^2\beta^2}{42a_0^3} \frac{\sqrt{5}}{\sqrt{4\pi}} p_2^0 [8 h_{f\to h}^{0,3} - \tfrac{4}{33} g_{f\to h}^{2,5} - \tfrac{8}{3} h_{f\to h}^{2,5} - \tfrac{40}{429} g_{f\to h}^{4,7} - \tfrac{196}{33} h_{f\to h}^{4,7} - \tfrac{7840}{429} h_{f\to h}^{6,9}] \ , \tag{13}$$

with

$$g_{f\to l}^{n,m} = \int_0^\infty dr_1 \frac{u_f^0(1)^2}{r_1^m} \int_0^{r_1} r_2^n u_f^0(2) u_{f\to l}^{(1)}(2) dr_2 \tag{14}$$

and

TABLE I. List of the integrals $g^{n,n+3}_{f\to l}$ and $h^{n,n+3}_{f\to l}$ required for the evaluation of D_{ss} for Gd^{3+}.

n	$g^{n,n+3}_{f\to p}$	$h^{n,n+3}_{f\to p}$	$g^{n,n+3}_{f\to f}$	$h^{n,n+3}_{f\to f}$	$g^{n,n+3}_{f\to h}$	$h^{n,n+3}_{f\to h}$
0		−0.993 68	−0.165 08	−0.113 62		0.027 47
2	−0.815 59	−0.904 35	−0.090 22	−0.073 43	0.005 55	0.011 61
4	−0.637 20		−0.060 29	−0.052 47	0.004 10	0.006 90
6						0.004 82

$$h^{n,m}_{f\to l}=\int_0^\infty dr_2\frac{u_f^0(2)}{r_2^m}u^{(1)}_{f\to l}(2)\int_0^{r_2}r_1^n[u_f^0(1)]^2dr_1 \ . \tag{15}$$

In the above equations, p_2^0 is expressed in units of $e^2/2a_0^3$ (a_0 denotes the Bohr radius), u_f^0 is r times the radial part of the free-ion f orbitals, and $u^{(1)}_{f\to l}$ are r times the radial part of the perturbation $\delta\psi_m(i)$ of the ith electron such that

$$\delta\psi_m(i)=p_k^0\sum_{l=|3-k|}^{3+k}(-1)^m\left[\frac{(2k+1)7(2l+1)}{4\pi}\right]^{1/2}\begin{bmatrix}k & 3 & l\\ 0 & m & -m\end{bmatrix}\begin{bmatrix}k & 3 & l\\ 0 & 0 & 0\end{bmatrix}Y_l^m(\theta_i,\phi_i)\frac{1}{r_i}u^{(1)}_{f\to l}(r_i) \ . \tag{16}$$

To employ Eqs. (10)—(16) for estimating the splitting in Gd^{3+} [$^7f(^8S)$] one needs to first obtain the radial wave functions $u^{(1)}_{f\to l'}$ occurring in the integrals (14) and (15). To this end, we have solved numerically the differential equations (8) adopting Numerov's method and using the Hartree-Fock 4f orbitals of Gd^{3+} calculated by Freeman and Watson.[15] In Fig. 1 we have plotted $u^{(1)}_{f\to p}$ so obtained as a function of r for Gd^{3+}. The other functions $u^{(1)}_{f\to f}$ and $u^{(1)}_{f\to h}$ are relatively too small in magnitude to be plotted in the same figure and therefore have not been shown. One notes in Fig. 1 that $u^{(1)}_{f\to p}$ has four nodes. Now, analyzing in terms of the number of nodes i.e., $N-l-1$, we deduce for p excitations ($l=1$) that the effective principal quantum number N should be 6, a result which reveals that the dominant character of the excitation comes from the 6p state. This is very gratifying since it shows that the contributions such as those from Eq. (1) seem to be present as a dominant part of many p excitations in $D_{ss}(f\to p)$, as expected.

The calculated $u^{(1)}_{f\to l'}$ radial functions are then used to evaluate the required integrals $g^{n,m}_{f\to l}$ and $f^{n,m}_{f\to l}$, which have been listed in Table I. As for the crystal field p_2^0 for Gd^{3+} in lanthanum ethyl sulfate, we have taken the same value as assumed by Wybourne and others in order to facilitate comparison with the available calculations, particularly with Wybourne's analysis of the zero-field splitting. Accordingly, identifying the p_2^0 with the relevant crystal-field value adopted carefully by Wybourne,[14] we have

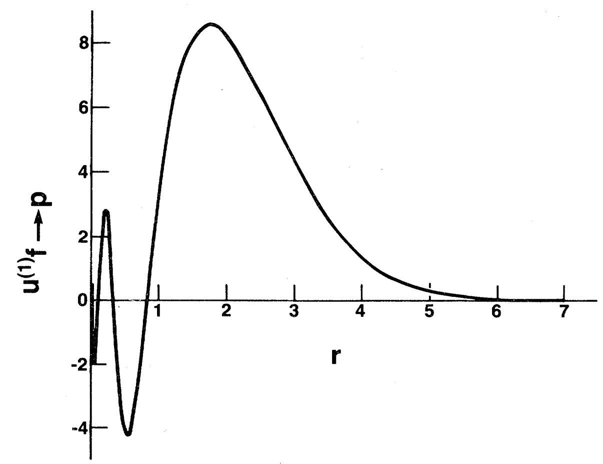

FIG. 1. Plot of the calculated $u^{(1)}_{f\to p}$ perturbation function as a function of r for Gd^{3+}.

$$p_2^0=-2.324\times10^{-3}(\sqrt{4\pi}e^2/2\sqrt{5}a_0^3) \ , \tag{17}$$

where we have used our calculated value $\langle r^2\rangle=0.7846a_0^2$, appropriate to the ground-state Gd^{3+} wave function.[15]

We now readily evaluate expressions (11)—(13) to obtain

$$\begin{aligned}&D_{ss}(f\to p)=+14.72\times10^{-4}\ \text{cm}^{-1}\ ,\\ &D_{ss}(f\to f)=+0.32\times10^{-4}\ \text{cm}^{-1}\ ,\\ &D_{ss}(f\to h)=0.38\times10^{-4}\ \text{cm}^{-1}\ ,\\ &D_{ss}(\text{total})=+15.42\times10^{-4}\ \text{cm}^{-1}\ ,\end{aligned} \tag{18}$$

which is of correct sign and is nearly one-fourth of the experimental value[16] of $+68.2\pm0.7\times10^{-4}$ cm^{-1} for Gd^{3+} in lanthanum ethyl sulfate.

According to the original estimates by Wybourne, the other mechanisms (mentioned earlier) have either yielded negligible contributions or contributions of right magnitude but of wrong sign. The mechanisms which give negligible contributions are (1) the third-order spin-spin mechanism[14] acting within the 4f^7 configuration, (2) the mechanism[14,17] involving configuration mixing by crystal fields, (3) the correlation crystal-field mechanism,[14,18] and (4) the configuration-interaction mechanism.[14] The two groups of mechanisms which yield individually contributions of wrong sign, though of correct order of magnitude, are (1) the fourth-order mechanism[16] which is linear in crystal field and cubic in spin-orbit interaction and fourth-order mechanism[16,19] quadratic in crystal field and spin-orbit interaction, and (2) the second-order relativistic mechanism.[14,20]

Later, it was shown[21] with the superposition model that Wybourne's major contributions have the same sign as the observed results; also, another mechanism, the spin-correlated crystal-field mechanism,[22] has been found to contribute significantly to D. It must be remarked, however, that the superposition model is based on a parametrization scheme and its results must be relied upon cautiously.

It is evident that the spin-spin contribution in the presence of an axial field of rank 2 is very significant and crucial for understanding the origin of the zero-field splitting of the $^7f(^8S)$-state ions, and hence should not be neglected when combining contributions from other mechanisms.[13,14] Furthermore, our calculations have revealed that the spin-spin mechanism involving axial fields of ranks 4 and 6 contributes vanishingly to D, a result which can also be established by group-theoretical arguments by writing an expression similar to Eq. (1) and noting that the matrix elements of H_{ss} between the ^{8}S state and the allowed intermediate states do not exist. We have been able to also derive the expressions due to the spin-spin interaction for the rhombic-field-splitting parameter E in the spin Hamiltonian $H_s = E(S_x^2 - S_y^2)$, the contributions of which in relation to D may be expressed as

$$E_{ss}(f \to l') = \frac{\sqrt{6}}{2} \frac{(p_2^2 + P_2^{-2})}{p_2^0} D_{ss}(f \to l') , \qquad (19)$$

with $p_k^{m_k}$ as the crystal-field parameters defined by

$$V_k^{m_k} = -p_k^{m_k} \sum_i r_i^k Y_k^{m_k}(\theta_i, \theta_i) \qquad (20)$$

as a generalization of Eq. (3), $l' \equiv p, f$, and h, and

$$E_{ss} = \sum_{l'} E_{ss}(f \to l') , \qquad (21)$$

similar to Eq. (10). Relation (19) can also be established by means of the Wigner-Eckart theorem.

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

[2] A. S. Chakravarty, J. Chem. Phys. 39, 1004 (1963).

[3] R. R. Sharma, T. P. Das, and R. Orbach, Phys. Rev. 149, 257 (1966); 171, 378 (1968); see also Ref. 6 for the improved value of D for Mn^{2+} and MnF_2 and ZnF_2 using the correct value of $10Dq$.

[4] R. R. Sharma, Phys. Rev. 176, 467 (1968).

[5] C. Hofer and R. R. Sharma, Phys. Rev. B 3, 696 (1971).

[6] R. R. Sharma, J. Appl. Phys. 42, 1572 (1971).

[7] J. A. Hodges, J. L. Dormann, and H. Makram, Phys. Status Solidi 35, 53 (1969).

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

[9] C. V. Stager, Can. J. Phys. 46, 807 (1968); to resolve the controversy in this paper refer to R. R. Sharma, Can. J. Phys. 47, 1185 (1969).

[10] R. R. Sharma, Phys. Rev. B 2, 3316 (1970).

[11] F. Holuj, S. M. Quick, and M. Rosen, Phys. Rev. B 6, 3169 (1972).

[12] W. Karthe, Phys. Status Solidi B 81, 323 (1977).

[13] For the review of the zero-field splitting of S-state ions, see R. R. Sharma, in *Advances in Mössbauer Spectroscopy*, edited by B. V. Thosar, P. K. Ayanger, J. K. Srivastava, and S. C. Bhargava (Elsevier, New York, 1983).

[14] B. G. Wybourne, Phys. Rev. 148, 317 (1966).

[15] A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962).

[16] C. A. Hutchison, Jr., B. R. Judd, and D. F. D. Pope, Proc. Phys. Soc. London, Sect. B 70, 514 (1957).

[17] K. Rajnak and B. G. Wybourne, J. Chem. Phys. 41, 565 (1964).

[18] D. J. Newman and S. S. Bishton, Chem. Phys. Lett. 2, 616 (1968).

[19] B. R. Judd, thesis, Oxford University, 1955.

[20] B. G. Wybourne, J. Chem. Phys. 43, 4506 (1965).

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

[22] G. G. Siu and D. J. Newman, J. Phys. C 15, 6753 (1982).