TABLE VI. Hyperfine-interaction elements for the two chlorine sites.

Element	Axis orientation	Value ($\times 10^{-4}$ cm^{-1})
$A_{xx}{}^{\text{I}}$	Mn-O$_1$	1.34
$A_{yy}{}^{\text{I}}$	⊥ to other two	···
$A_{zz}{}^{\text{I}}$	Mn-Cl$_1$	1.08
$A_{xx}{}^{\text{II}}$	⊥ to other two	···
$A_{yy}{}^{\text{II}}$	c	1.16
$A_{zz}{}^{\text{II}}$	Mn-Cl$_2$	···

elements one must estimate the value of the spin at 0°K. We have previously noted that the proton resonance gives $S(0°)\simeq\frac{5}{2}$ which is consistent with the specific-heat results of Miedema *et al.*[19] Values of the components of the hyperfine-interaction tensor are given in Table VI. The difference in the $\mathbf{A}$ components for the Cl$_1$ sites may be taken as an indication of the p-orbital contribution. It is interesting to try to compare the order of magnitude of the components we obtain with those given by Shulman and Jaccarino[20] for MnF$_2$. On reducing their value by the ratio

$$\frac{(\gamma_n)_{\text{Cl}}|\psi_{3s}(0)|^2{}_{\text{Cl}}}{(\gamma_n)_{\text{F}}|\psi_{2s}(0)|^2{}_{\text{F}}},$$

one obtains $\mathbf{A}\sim 2.6\times 10^{-4}$ cm^{-1}. The agreement with our results is probably satisfactory since the Mn-cation distance is 2.11 Å in MnF$_2$ and 2.5 Å in MnCl$_2\cdot$4H$_2$O.

ACKNOWLEDGMENTS

The authors take pleasure in acknowledging a number of very helpful suggestions from Dr. E. H. Carlson, Dr. J. A. Cowen, Dr. P. M. Parker, and Dr. H. Forstat. We should also like to thank R. Au for calculating the various dipolar sums and Jan Hessler for help in collecting the data. Special thanks are to be accorded Dr. Z. M. El Saffar for providing us with neutron-diffraction data on the proton positions.

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[19] A. R. Miedema, R. F. Wielinga, and W. J. Huiskamp, Physica **31**, 835 (1965).

[20] R. G. Shulman and V. Jaccarino, Phys. Rev. **108**, 1219 (1957).

PHYSICAL REVIEW VOLUME 149, NUMBER 1 9 SEPTEMBER 1966

Nonvanishing Electric Field Gradients, Zero-Field Splitting, and Magnetic Field Energies of ^6S-State Ferric Ion in Tetragonal Symmetry

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(Received 17 February 1966)

A calculation has been made of the spin-orbit coupling of the high-spin ground state of ferric ion, the ^6S state, with excited doublet and quartet electronic states in strong crystal electric fields of tetragonal symmetry. The aim of the calculation was to simulate as closely as possible, without explicitly including bonding, the condition of ferric ion in the heme group of ferriheme compounds. Eigenfunctions and eigenvalues resulting from such a calculation were used as a basis for calculating other properties of interest of the ferric ion in such systems. Explicitly, the zero-magnetic-field splitting of the sextet ground state, magnetic-field energy components, effective magnetic moments, and the lattice and valence contributions to an electric-field gradient at the iron nucleus were calculated. These properties were investigated as a function of the cubic and tetragonal field strengths, the spin-orbit coupling strength, and the number of excited states included in the interaction. The calculated results were compared with existing experimental data from single-crystal electron spin resonance, magnetic-suceptibility measurements, and the observed quadrupole splitting of the Mössbauer resonance of high-spin ferriheme compounds. For a consistent and relatively narrow range of values for input parameters, all of the calculated properties agreed quite well with the experimental results currently available.

FERRIC ion in six-coordinated hemoglobin complexes with such ligands as H$_2$O and F$^-$ in the sixth position, has a Mössbauer resonance (MR) spectrum which is split by the interaction of a nuclear quadrupole moment of the excited state of Fe^{57} with a residual electric field gradient (EFG) at its nucleus.[1] Also, electron-spin-resonance (ESR) data indicate a nontrivial splitting of the ^6S ground state into three doubly degenerate components.[2]

These properties are not immediately apparent for an "S-state" ion. Such a ground state is not split by a crystal electric field. Nor is it split by first-order spin-orbit interaction of its six multiplet partners. Nor can the electron distribution of this $3d^5$ spherically symmetric state, by itself, contribute to a nonzero EFG at the nucleus.

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[1] J. Maling and M. Weissbluth, in *Electronic Aspects of Biochemistry*, edited by B. Pullman (Academic Press Inc., New York, 1964).

[2] D. J. E. Ingram, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), Vol. II.

TABLE I. Calculated results which explain ESR and Mössbauer resonance observations.

Δ (cm^{-1})	20 000	22 000	22 000	24 000	24 000	24 000
μ (cm^{-1})	5000	4000	5000	3000	4000	5000
ΔE_1 (cm^{-1})	4.32	4.38	7.20	4.16	7.64	14.28
ΔE_2 (cm^{-1})	8.91	9.30	15.25	9.67	17.55	33.25
$g_{\parallel}$	1.998	1.998	1.998	1.998	1.996	1.996
$g_{\perp}$	5.990	5.97	5.98	5.98	5.97	5.95
$\Delta g_{\perp}{}^{6000}$ (%)	3.3	3.0	1.2	3.6	1.06	0.30
μ_{eff} (Bohr magnetons)	5.84	5.84	5.79	5.83	5.77	5.65
q_1 (esu/cm^3)$\times 10^{+14}$	24.91	19.93	24.91	14.95	19.93	24.91
q_2	1.24	1.44	2.80	1.71	3.72	9.01
$q=q_1-q_2$	23.66	18.49	22.11	12.88	16.21	15.99
Q_{exp} (barns)	0.275	0.35	0.293	0.491	0.401	0.41

A possible mechanism to explain these observed effects is to assume spin-orbit coupling interaction and consequent mixing of the ground state with excited electronic states of the $3d^5$ configuration in a strong electric field of tetragonal symmetry created by the surrounding ligands. Such mixing with nonspherical excited states is certainly possible. To investigate whether, based on this model, the actual magnitude of the observed effects could be explained, a detailed numerical calculation was made.

Spin-orbit matrix elements in strong D_4 crystal fields were calculated by irreducible tensor methods.[3] These matrix elements, together with selected values of cubic field strength in the range 10 000–40 000 cm^{-1}, tetragonal distortions of magnitude 1000–5000 cm^{-1}, and spin-orbit coupling parameters of 150–600 cm^{-1}, were used as input to a matrix diagonalization program with different numbers of basis set functions until addition of more did not change the results appreciably. It turns out that the results for a set of 12 and for a set of 33 basis states are not appreciably different. Electrostatic-energy parameters were not varied, nor were covalent effects explicitly considered.

Eigenvalues and eigenfunctions of the spin-orbit matrix were obtained which yielded immediately a zero-field splitting of the high-spin $^6A_1$ ground state into three doubly degenerate components. These spin-orbit mixed eigenstates were used as a basis set for the calculation of the other properties of the system of interest, such as magnetic field energies, electric field gradients, magnetic moments and their temperature dependence. The details of the calculation and the sensitivity of the results to the variation of the four starting conditions mentioned above, will be discussed elsewhere. The results we wish to report here are for a reasonable value of spin-orbit coupling strength, i.e., the experimentally determined free-ion value of 420 cm^{-1} and for the most extensive calculation explored here, namely a mixing of 33 doubly degenerate electronic states. Under these conditions, we have been able, with consistent values of field-strength parameters, to explain and correlate several observed properties of the high-spin ferric ion in six-coordinated heme complexes of essentially tetragonal symmetry, to within the accuracy and detail currently available experimentally.

Electron-spin-resonance data for single crystals of high-spin ferric heme complexes with H_2O or F^- as the sixth ligand have been reported by Ingram and coworkers.[2] They observe one transition with a $g_{\parallel}=2.00$ and a $g_{\perp}=6.00$ (± 0.05), for frequencies up to 50 000 Mc/sec, with $g_{\parallel}$ linear in this region.

From the observed region of proportionality of z field and frequency, we estimate a minimum zero-field splitting $\Delta E_1 = E(^6A_1\tfrac{3}{2}) - E(^6A_1\tfrac{1}{2})$ of 3.39 cm^{-1}, corresponding to a value of $D=1.7$ cm^{-1} in the spin Hamiltonian. Nothing can be gleaned experimentally about the second energy interval $\Delta E_2 = E(\tfrac{5}{2}) - E(\tfrac{3}{2})$. This estimate of the minimum value of D is lower than that of 5 cm^{-1} which has previously been quoted as necessary to explain experimental data.[4]

To explain the observed ESR results then, our model must yield energy levels sufficiently perturbed from their original values to give a high enough value of ΔE_1 and yet give eigenfunctions which have relatively little mixing, thus preserving M_s as a good quantum number. Within the large range of field-strength parameters studied, only a small range of values of cubic and tetragonal field strengths gave the minimum value of ΔE_1. For the six sets of parameters within this range for which ΔE_1 was calculated, values of $g_{\parallel}$ and $g_{\perp}$ were also calculated and gave excellent agreement with experiment.

Calculated values of ΔE_1, ΔE_2, $g_{\parallel}$, and $g_{\perp}$ for six possible values of field parameters that explain ESR results are given in Table I. We have also calculated deviations from linearity in $g_{\perp}$ as a function of $H_{\perp}$, which can mix the final states. An H_z field does not mix these states in any order. To compare our calculated behavior of $g_{\perp}$ for the sets of field values that explain the other ESR data, we have made use of preliminary work on polycrystalline solids of the high-

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[3] J. S. Griffith, *The Irreducible Tensor Method for Molecular Symmetry Groups* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962).

[4] J. S. Griffith and M. Kotani, in *Quantum Aspects of Polypeptides and Polynucleotides*, edited by M. Weissbluth (Interscience Publishers, Inc., New York, 1964).

spin H_2O and F^- ferrihemoglobin complex.[5] In this work only one value of g equal to 5.90 ± 0.05 was reported. The linearity of this value was measured for frequencies up to 1.67 cm^{-1}, corresponding to an $H_\perp$ field of approximately 6000 G. Small deviations from linearity were obtained on the low side of 5.95 which at 6000 G appear to be $\leq 3\%$. In Table I, we give the percent deviation from linearity, $\Delta g_\perp{}^{6000}$, at 6000 G which we have calculated for the six points that fit other data. We see that these also are all within the scope of the results reported.

Effective magnetic moments were also calculated for these points at three different temperatures, and the results at $kT=200$ cm^{-1} are given in Table I for the six possible values of field parameters that explain the ESR results. We see that the magnetic moments calculated are in good agreement with the experimentally observed room-temperature values of 5.8–5.9 reported for these compounds.[2]

Thus we may conclude that our model can, with a narrow range of possible parameters, explain both a lower minimum value of zero-field splitting than heretofore considered, and observed g values for high-spin ferric ion complexes, as well as room-temperature magnetic susceptibility measurements. We have calculated the position of other possible ESR transitions and the temperature dependence of the magnetic moments, and EFG. No experimental data is however currently available with which to compare these results.

To further test the validity of this model and to perhaps narrow the choice of parameters, we ask whether among the six sets of results which explain the ESR data, there are any that can also account for the observed magnitude of the Mössbauer resonance splitting. This value of $\Delta E=2$ mm/sec observed for ferric ion in methemoglobin is 2–4 times the value observed for ferric ion in the octahedral and tetrahedral sites of rare-earth iron garnets and in Fe_2O_3.[6] Assuming tetragonal symmetry, which is consistent with the ESR results, $\Delta E=\frac{1}{2}eqQ$, where q is the z component of electric-field gradient and Q is the nuclear quadrupole moment of the excited $I=\frac{3}{2}$ state. Unfortunately Q is not known exactly. The procedure which has been followed in the past for the other ferric systems is to measure ΔE and calculate q based on a lattice contribution only.[7] Then from these two quantities a value of Q is calculated. While Q should be constant from system to system, values of Q calculated for the three systems mentioned had a range of 0.185 to 0.487 b,[6,7] due to both experimental and theoretical uncertainties.

We have calculated total values of q including the direct contribution from the lattice and also a valence-electron contribution from all electronic states within kT of the ground state. This latter term has always been assumed zero for S-state ions and has never been calculated for ferric ion. Including both these contributions the total expression for q is: $q=(1-R)\langle r^{-3}\rangle q_{\text{val}}+(1-\gamma_\infty)\langle r^2\rangle q_{\text{lat}}$. Using values of $(1-\gamma_\infty)=10.14$; $\langle r^2\rangle=1.4$ a.u.; $(1-R)\langle r^{-3}\rangle=3.3-4.0$ a.u.,[8] the expression for q becomes: $q=4.98\times10^{11}\ \mu(\text{cm}^{-1})-1.297\times10^{16}\ V_{zz}(T)$ where μ is the tetragonal field strength and $V_{zz}(T)$[9] is the contribution to the z component of the electric-field gradient from all electronic states within 2000 cm^{-1} of the ground state. From this expression, we calculated total values of q for the same six sets of parameters as shown in Table I. While the valence contribution is in each case small compared to the lattice contribution, it is by no means negligible. These separate lattice and valence contributions are labeled as q_1 and q_2, respectively, in the tables with the total $q=q_1-q_2$. As has been done in the past, from the calculated values of q, this time with a valence contribution, and the measured value of ΔE, we calculated values for the nuclear quadrupole moment Q. These are also given in Table I for the six ESR-consistent values of field parameters. We see that in all except perhaps one instance, they fall within the previously calculated range of Q's. We must await a more precise evaluation of the value of Q before we can select the best fit among these possibilities and also before we can evaluate the extent of the valence-electron contribution, whose relative magnitude now is within the range of ambiguity in values of Q.

Thus we conclude that from a strong tetragonal field spin-orbit interaction of the sextet S ground state of ferric ion, we obtain a description of the high-spin system which explains, with consistent values of parameters, both the existing ESR results and Mössbauer resonance results within the ambiguity still existing in the experimental observations.

Further elucidation awaits more experimental observation.

This work was supported by an Office of Naval Research Contract No. NONR 25(87).

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[5] J. E. Bennett, D. J. E. Ingram, P. George, and J. S. Griffith, Nature **176**, 394 (1955).

[6] C. Alff and G. K. Wertheim, Phys. Rev. **122**, 1414 (1961).

[7] G. Burns, Phys. Rev. **124**, 524 (1961).

[8] R. Ingalls, Phys. Rev. **128**, 1155 (1962).

[9] $$V_{zz}(T)=\sum_N V_{zz}(N,N)e^{-E_N/kT},$$
where $$V_{zz}(N,N)=\langle N|3\cos^2\theta-1|N\rangle.$$
E_N is the energy of Nth eigenstate relative to the ground state, sum is over all $E_N\leq2000$ cm^{-1}.