

Electronic and magnetic structure of α -FeSO₄*

Reinhart Zimmermann

Physikalisches Institut II, Universität Erlangen, 852 Erlangen, West Germany

Alfred Trautwein

Angewandte Physik, Universität des Saarlandes, 66 Saarbrücken, West Germany

Frank E. Harris

Department of Physics, University of Utah, Salt Lake City, Utah 84112

(Received 27 March 1975)

The study of the electronic and magnetic structure of α -FeSO₄ is based on a model which consists of iron surrounded by six SO₄ tetrahedra forming a [Fe(SO₄)₆]⁻¹⁰ cluster; its three-dimensional structure is based on x-ray diffraction data. For many-electron terms of ferrous high-spin compounds derived from semiempirical cluster calculations, we investigate spin-orbit coupling, electric field gradient (EFG), and susceptibility. In particular for the EFG we discuss valence, overlap, and lattice contributions. Within the paramagnetic region of α -FeSO₄ we investigate the orientation of the EFG with respect to the crystallographic frame, the Mössbauer parameters ΔE_Q and η , and the susceptibility; we find our results in reasonable agreement with the recent experimental data of Wehner. Within the antiferromagnetic region at 4.2 K we study the influence of the molecular exchange field upon EFG, ΔE_Q , and η , and we further estimate the orientation of the internal magnetic field (H_{int}) at the iron nucleus with respect to the crystallographic frame. Finally we derive an angle of 27.7° between H_{int} and the main component of the EFG. Our low-temperature study of α -FeSO₄ agrees with the recent experimental findings of Wehner, but it disagrees with those of Ono and Ito.

I. INTRODUCTION

Iron sulfate has been the subject of Mossbauer,¹⁻³ susceptibility,⁴ x-ray-diffraction,⁵ and neutron-diffraction⁶ measurements. For a careful investigation of FeSO₄ it is necessary to take into account effects which depend on aging or temperature treatment of the probe. The study of α -FeSO₄ by Wehner³ shows results which deviate from FeSO₄ results found by Ok² and Ono and Ito,¹ indicating that Ok might have been concerned with the additional high-temperature phase γ -FeSO₄, while Ono and Ito's spectral parameters are limited by the relatively large statistical error in their low-temperature spectrum of FeSO₄.³

On the basis of Samaras and Coing-Boyat's x-ray data⁵ on α -FeSO₄, and a semiempirical molecular-orbital (MO) treatment of paramagnetic systems, which was described previously,⁷ we derive many-electron wave functions for the complex under study. These many-electron terms are then used to calculate their mutual spin-orbit interaction, the temperature-dependent electric field gradient V_{pq} (quadrupole splitting ΔE_Q , asymmetry parameter η , and the orientation of V_{pq} with respect to the crystallographic framework), and the susceptibility χ_{pq} . Finally, we derive the low-temperature properties of α -FeSO₄ and compare our theoretical results with the experimental findings of Wehner.³

II. MOLECULAR MODEL FOR α -FeSO₄

α -FeSO₄ was represented in our calculations by iron surrounded by six SO₄ tetrahedra forming a

[Fe(SO₄)₆]⁻¹⁰ complex. We used atomic coordinates as found by Samaras and Coing-Boyat⁵ from x-ray-diffraction measurements of α -FeSO₄. Within the limit of the linear combination of atomic orbitals (LCAO) MO calculations the atomic basis orbitals for valence electrons were Slater-type orbitals (STO) 3*d*, 4*s*, and 4*p* for iron, 2*s* and 2*p* for oxygen, and 3*s* and 3*p* for sulfur. However, since α -FeSO₄ is paramagnetic (high-spin ferrous) we are concerned with many-electron terms rather than with single-electron molecular orbitals. Therefore, after inclusion of spin, we use the Hückel LCAO MO's to construct antisymmetrized products (Slater determinants) for the various *N*-electron terms under study. Additionally we take into account Coulomb interaction and spin-orbit coupling. The corresponding theoretical treatment for ferrous high-spin iron complexes is described in Sec. III.

III. SPIN-ORBIT COUPLING, ELECTRIC FIELD GRADIENT, AND SUSCEPTIBILITY FOR FERROUS HIGH-SPIN IRON

A. General

In LCAO MO theory the molecular orbitals $|k\rangle$ are linear combinations of atomic orbitals (AO's) $|h\rangle$

$$|k\rangle = \sum_n a_{kh} |h\rangle, \quad k, h = 1, 2, 3, \dots \quad (1)$$

With electron-spin orbitals $|n\rangle = |+\rangle, |-\rangle$ the MO's are extended to molecular spin orbitals (MSO),

$$|k^{(n)}\rangle = |k\rangle |n\rangle. \quad (2)$$

The various N -electron configurations $|k_1^{(n_1)}, \dots, k_N^{(n_N)}\rangle$ are Slater determinants of MSO's. Each of the 25 ferrous high-spin terms ($S=2$) can be described by the doubly occupied molecular orbital of mainly $3d$ character, $|k\rangle$, and by the azimuthal quantum number m of total spin S . For $m=2$ these terms are simply expressed by

$$|S=2; k, m=2\rangle = |\dots, k^{(+)}, k^{(-)}, k_1^{(+)}, k_2^{(+)}, k_3^{(+)}, k_4^{(+)}\rangle, \quad (3)$$

where the molecular orbitals, $|k_i\rangle$ ($i=1, 2, 3, 4$) are the remaining singly occupied MO's of mainly $3d$ character. The ellipsis refers to closed shells. The terms $|S=2, k, m\rangle$ with $m=1, 0, -1, -2$ are then obtained by the application of the step-down operator \hat{S}^- to Eq. (3).⁸ The eigenvectors of the Hamiltonian including Coulomb interaction, $|l, m\rangle$, are linear combinations of configurations with the same quantum number m , since the spin-independent Coulomb interaction can mix only terms with equal spin S ,

$$|l, m\rangle = \sum_{k=1}^5 b_{lk} |S=2; k, m\rangle, \quad (4)$$

where the coefficients b_{lk} are independent of m and result from configuration-interaction (CI) calculations as described previously.⁷ However, the inclusion of spin-orbit coupling \hat{H}_{SO} may lead to considerable mixing of CI terms. The resulting eigenvectors $|e_\alpha\rangle$ of this problem are again linear combinations

$$|e_\alpha\rangle = \sum_{l, m} C_{\alpha lm} |l, m\rangle. \quad (5)$$

The coefficients $C_{\alpha lm}$ and energies E_α are obtained from diagonalization of the total Hamiltonian including spin-orbit coupling; the matrix elements $\langle l', m' | \hat{H}_{SO} | l, m \rangle$ will be discussed below. Since we are interested in susceptibilities χ and electric field gradients V we calculate for each $|e_\alpha\rangle$ its relevant χ_{pq} and V_{pq} tensor ($p, q=x, y, z$). The procedure for this calculation is based on the properties of one-electron operators

$$Q = \sum_{\text{electrons } i} q_i, \quad (6)$$

where q_i acts only on the i th electron.

For operators Q independent of spin the matrix elements are diagonal within spin

$$\langle l', m' | Q | l, m \rangle = \langle l' | Q | l \rangle \delta_{m'm}. \quad (7)$$

The quantities $\langle l' | Q | l \rangle$ can be calculated for any m value, in the easiest case for $m=2$ [Eq. (3)]. Since q_i is acting on the i th electron only, we obtain⁸⁻¹⁰

$$\begin{aligned} \langle l' | Q | l \rangle &= \left(\sum_{\bar{k}} a \langle \bar{k} | q | \bar{k} \rangle \right) \delta_{ll'} \\ &+ \sum_{k', k=1}^5 b_{l'k'} b_{lk} \langle k' | q | k \rangle, \end{aligned} \quad (8)$$

where the sum over \bar{k} includes all occupied MO's. The factor a takes either the value two for all MO's of non- $3d$ -type or the value one for the five MO's with mainly Fe $3d$ character. By application of Eq. (1) the matrix elements $\langle \bar{k} | q | \bar{k} \rangle$ and $\langle k' | q | k \rangle$ in Eq. (8) can be expressed in terms of atomic-orbital matrix elements. With

$$\begin{aligned} c_{(l' l)(h' h)} &= \left(\sum_{\bar{k}} a_{\bar{k}h'} a_{\bar{k}h} \right) \delta_{l'l} \\ &+ \sum_{k', k} b_{l'k'} a_{k'h'} b_{lk} a_{kh} \end{aligned} \quad (9a)$$

we obtain

$$\langle l' | Q | l \rangle = \sum_{h', h} c_{(l' l)(h' h)} \langle h' | q | h \rangle. \quad (9b)$$

The sum in Eq. (9b) consists of an iron part (h and h' both iron AO's), an overlap part (h an iron AO and h' a ligand AO and vice versa), and a ligand part (h and h' both ligand AO's). These parts are handled differently as indicated by their significance in the present study.

B. Approximations

The approximations used for calculating spin-orbit coupling, susceptibility, and electric field gradient from Eq. (9b) are the following.

Spin-orbit coupling: Assuming that the spin-orbit functions $\xi_A(r_{iA})$,¹¹ with r_{iA} the distance between electron i and the nucleus of ion A , are extremely localized, we omit overlap parts and obtain

$$\begin{aligned} \langle l', m' | \hat{H}_{SO} | l, m \rangle &= -\frac{1}{2S} \left(\sum_A \sum_{h', h \in A} c_{(l' l)(h' h)} \right. \\ &\left. \times \langle h' | \xi_A(r_A) \hat{L}_A | h \rangle \right) \cdot \langle m' | \hat{S} | m \rangle. \end{aligned} \quad (10)$$

The symbol $(h', h \in A)$ in Eq. (10) means that we have to sum over all AO's h', h of ion A . For the $3d$ shell of ferrous high-spin iron we take

$$-(1/2S) \langle h'_{3d} | \xi(r_{Fe}) \hat{L}_{Fe} | h_{3d} \rangle = \lambda_{Fe, 3d} \langle h' | \hat{L}_{Fe} | h \rangle. \quad (11)$$

Rather than using the free-ion value¹² of -103 cm^{-1} , $\lambda_{Fe, 3d}$ was corrected according to the actual electron density within the AO's.

Susceptibility: The χ tensor is obtained from

$$\chi_{pq} = \mu_B^2 A \sum_{\alpha', \alpha} \langle e_\alpha | \hat{L}_p + 2\hat{S}_p | e_{\alpha'} \rangle$$

$$\times \langle e_{\alpha'} | \hat{L}_q + 2\hat{S}_q | e_{\alpha} \rangle \frac{e^{-E_{\alpha}/kT} - e^{-E_{\alpha'}/kT}}{E_{\alpha'} - E_{\alpha}}, \quad (12)$$

where A is the Avogadro number and μ_B the Bohr magneton. The orbital part¹³ of this equation can again be expressed by AO matrix elements according to Eqs. (5) and (9b).

Electric field gradient: In the limit of fast relaxation the electric-field-gradient (EFG) tensor V_{pq} is the thermal average of the EFG tensor operator \hat{V}_{pq} .

$$V_{pq} = \frac{\text{Tr}(\hat{V}_{pq} e^{-\hat{H}/kT})}{\text{Tr}(e^{-\hat{H}/kT})}, \quad p, q = x, y, z. \quad (13)$$

The operator \hat{V}_{pq} is the sum of single-electron operators $\hat{v}_{pq,i}$ of the i th electron, which have the form¹⁴

$$\hat{v}_{pq} = [1 - \gamma(r)] Ze(3pq - r^2 \delta_{pq})/r^5, \quad (14)$$

where Ze is the charge of an electron ($Z=1$) or of a ligand, and r follows from $r^2 = x^2 + y^2 + z^2$. The function $\gamma(r)$ is the quadrupole polarizability of the core electrons and is represented in terms of Sternheimer factors,^{14,15}

$$\gamma_{\infty} = \lim_{r \rightarrow \infty} \gamma(r) \quad (15)$$

and

$$R = \langle \gamma(r)r^{-3} \rangle / \langle r^{-3} \rangle. \quad (16)$$

Applying Eqs. (1)–(9) we have four types of AO matrix elements $\langle h' | \hat{v}_{pq} | h \rangle$.

(a) Matrix elements within an atomic shell of ferrous high-spin iron can be obtained by the operator equivalence¹⁶

$$\hat{V}_{pq} = \langle h | \hat{V} | h \rangle e(1-R) \langle r^{-3} \rangle \times \left\{ \frac{1}{2}(\hat{l}_p \hat{l}_q + \hat{l}_q \hat{l}_p) - \frac{1}{3}[l(l+1)] \delta_{pq} \right\}. \quad (17)$$

The reduced matrix element $\langle h | \hat{V} | h \rangle$ takes the value $\frac{2}{7}$ for d electrons, $\frac{6}{5}$ for p electrons, and 0 for s electrons. The quantity e represents the (positive) elementary charge. $\langle r^{-3} \rangle_{3d}$ is the radial factor with values 4.49 a.u. for Fe $3d^7$, 5.09 a.u. for Fe $3d^6$, and 5.73 a.u. for Fe $3d^5$.¹⁷ The Sternheimer shielding correction¹⁵ is taken as $(1-R)_{3d} = 0.68$. For Fe $4p$ electrons the quantity $(1-R)_{4p} \langle r^{-3} \rangle_{4p}$ is taken to be $\frac{1}{3}$ of the corresponding quantity for the $3d$ electrons.¹⁸

(b) Nondiagonal elements between different shells of iron, for example, between $3d$ and $4s$ AO's are neglected.

(c) Matrix elements of ligand AO's are approximated by

$$V_{pq} = (1 - \gamma_{\infty}) q_{1ig} \frac{3R_p R_q - R^2 \delta_{pq}}{R^5}. \quad (18)$$

For $(1 - \gamma_{\infty})$ we take 10.6.¹⁵ The charge q_{1ig} is obtained from MO calculations, and R_x , R_y , and R_z are the Cartesian coordinates of the ligands.

(d) The overlap part between iron and ligand AO's is estimated assuming that the overlap of the iron AO's and the ligand AO's at ion A is limited to a small region in which r may be taken as constant ($r = \bar{R}$),

$$V_{pq}^{ov} = e[1 - \gamma(\bar{R})] \frac{3\bar{R}_p \bar{R}_q - \bar{R}^2 \delta_{pq}}{\bar{R}^5} \times \sum_{h \in \text{Fe}, h' \in A} [c_{(II)(h'h)} + c_{(II)(hh')}] S_{h'h}. \quad (19)$$

The Sternheimer factor $1 - \gamma(r = \bar{R})$ is smaller than $1 - \gamma(r = R)$ because of decreasing antishielding with decreasing distance r . The r dependence of $1/r^3$ goes in the opposite direction. Since we do not know the correct radial dependence of $\gamma(r)$ we are within the approximation of (c) if we esti-

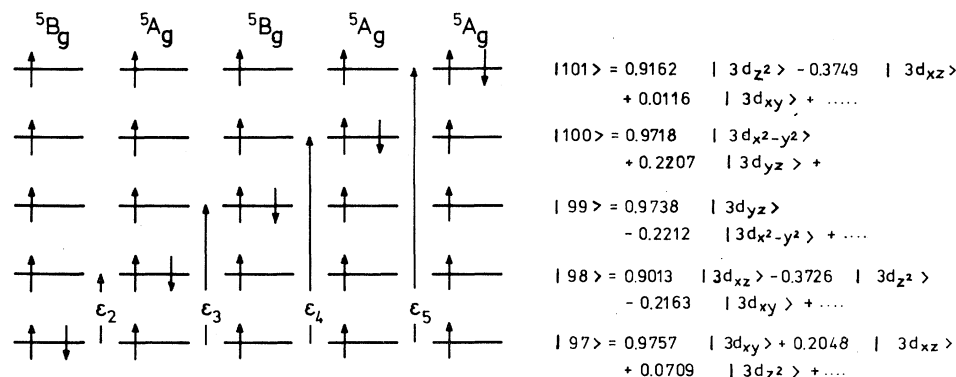


FIG. 1. Many-electron terms $|k\rangle$ which are used to calculate $V_{pq}(T)$ and $\chi_{pq}(T)$. The twofold axis of the C_{2h} point symmetry of the ferrous high-spin iron is parallel to our y axis. The ϵ_i are LCAO MO energies.

doubly occupied MO states $|k\rangle$, $k=1-96$

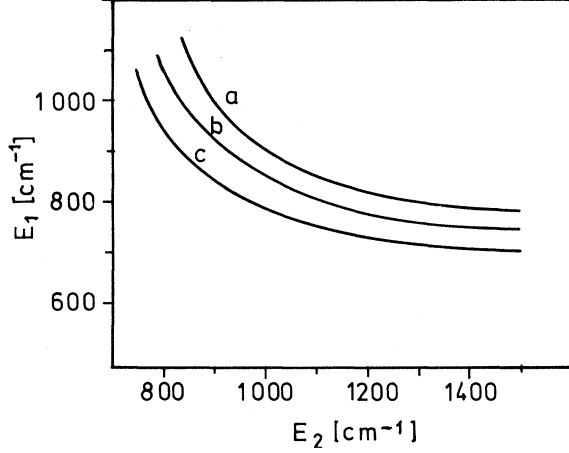


FIG. 2. Pairs of energies E_1 and E_2 for which we were able to fit ΔE_Q^{expt} (300 K); see text. Curves *a*, *b*, and *c* correspond to values of the spin-orbit coupling constant λ of -100 , -90 , and -80 cm^{-1} , respectively.

mate the overlap contribution by

$$V_{pq}^{ov} \approx e(1 - \gamma_\infty) \frac{3R_p R_q - R^2 \delta_{pq}}{R^5} \times \sum_{h \in F_e, h' \in A} (c_{(11)(h'h)} + c_{(11)(hh')}) S_{h'h}. \quad (20)$$

IV. RESULTS AND DISCUSSION

A. Paramagnetic region

For C_{2h} point symmetry of the central ferrous high-spin iron with the twofold axis along the crystallographic a axis of α -FeSO₄ we are concerned with five energetically low-lying terms,

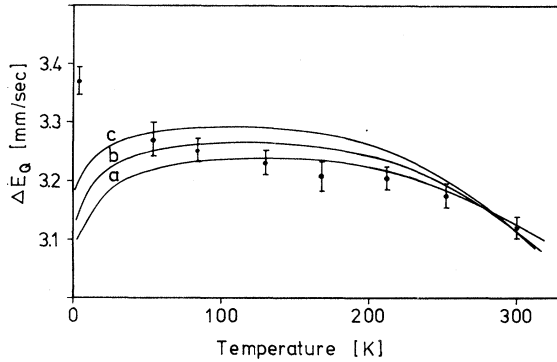


FIG. 3. Temperature-dependent quadrupole splitting, $\Delta E_Q(T)$. Experimental points for α -FeSO₄ are taken from Ref. 3. Solid curves are calculated as described in the text. Energies E_1 , E_2 , E_3 , E_4 , and E_5 in cm^{-1} and spin-orbit coupling constants λ in cm^{-1} corresponding to $\Delta E_Q(T)$ curves are: (a) 0, 850, 1050, 5000, 13 000, -100 , (b) 0, 750, 1150, 5000, 13 000, -90 , and (c) 0, 750, 1000, 5000, 13 000, -80 .

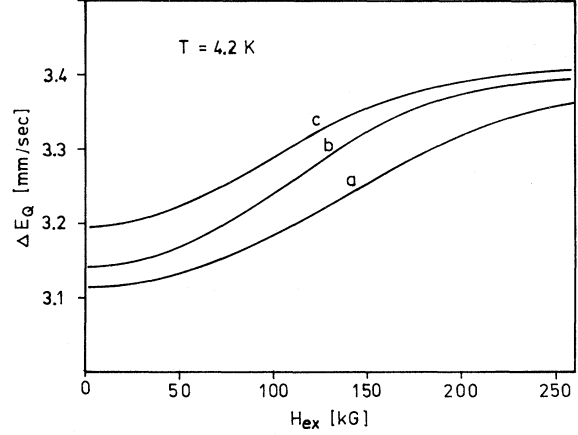


FIG. 4. Calculated quadrupole splittings, ΔE_Q , at 4.2 K depending on the magnitude of the exchange field, H_{ex} . Curves *a*, *b*, and *c* correspond to E_i and λ as given in Fig. 3.

three of symmetry 5A_g and two of symmetry 5B_g . In Fig. 1 they are given in terms of LCAO AO's $|k\rangle$ and spin populations $|n\rangle$. From CI calculations we find that configuration interaction between these five terms is negligible, i. e., the coefficient matrix b_{ik} of Eq. (4) is characterized approximately by $b_{ik} = \delta_{ik}$.

Calculating the EFG tensor for the ground state 5B_g along the lines described above we find a positive principal EFG component V_{zz} , and an asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz} = 0.2$, with $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$. The main component V_{zz} is characterized by polar angles $\theta = -16^\circ$ and $\varphi = 0^\circ$ within the frame $x=c$, $y=a$, and $z=b$; one of the principal axis (\hat{y}) is parallel to one of the crystallographic axis (a). From V_{zz} and η of the ground state 5B_g we derive a quadrupole splitting $\Delta E_Q({}^5B_g) = 3.6$ mm/sec. Comparing this value with the experimental results in the temperature range between 4.2 and 300 K we obviously have to take into account spin-orbit coupling between the five configurations of Fig. 1.

Since the LCAO treatment takes into account the electronic repulsion in an implicit way, the single-electron and Coulomb-repulsion energies may be taken as a first approximation for the energy separations E_i between configurations $|1, m\rangle$ and $|l, m\rangle$. With $\lambda = -100$ cm^{-1} , -90 cm^{-1} , and -80 cm^{-1} we find fits of the experimental quadrupole splitting $\Delta E_Q(300 \text{ K}) = 3.12 \pm 0.025$ mm/sec (Ref. 3) for various pairs of E_2 and E_3 (Fig. 2). The energies E_4 and E_5 were 5000 cm^{-1} and 13000 cm^{-1} , respectively, but can only be determined to within about 1000 cm^{-1} owing to the uncertainty in ΔE_Q . With the energies E_i of Fig. 2 we also calculate the temperature dependence of the quadrupole splitting $\Delta E_Q(T)$, and we find approximate fits in

the range between 77 and 300 K (Fig. 3). This result includes the assumptions: (a) that slight variations of E_2 and E_3 do not influence the CI terms, and (b) that the energies E_i are temperature independent.

The susceptibility χ of α -FeSO₄ follows at high temperatures a Curie-Weiss law

$$\chi = C/(T + \Theta),$$

with $C = 3.98$ emu/mol K the Curie constant and $\Theta = 30.5$ K the paramagnetic Curie temperature.⁴ The temperature Θ , which is different from the Néel temperature, depends on the difference of the exchange coupling constants within and between the two magnetic sublattices. The Curie constant C , however, reflects the magnetic properties of each ion alone, i. e., if the exchange interaction could be switched off, the susceptibility would be given by

$$\chi = C/T.$$

Thus we can obtain the Curie constant from our MO calculation in the paramagnetic region. It results in 3.75 emu/mol K, which agrees within 6% with the experimental value.

The disagreement of our calculated $\Delta E_Q(4.2$ K) value of 3.15 mm/sec with the measured quadrupole splitting at liquid-He temperature of 3.37 mm/sec finds a plausible explanation from inspection of the low-temperature properties of α -FeSO₄.

B. Antiferromagnetic region

At temperatures $T < 23.5$ K α -FeSO₄ is antiferromagnetic.⁴ From Mössbauer powder spectra at 4.2 K,³ information was obtained about the quadrupole splitting $\Delta E_Q(4.2$ K), the asymmetry parameter η , the magnitude of the internal magnetic field \vec{H}_{int} at the nuclear site of iron, and the orientation of \vec{H}_{int} relative to the main axis system of the EFG (polar angles θ^H and ϕ^H). Taking the neutron-diffraction result⁶ that the spin direction is parallel to the b axis and assuming in addition that one of the main axes of the EFG tensor is parallel to the twofold axis a ($\equiv \gamma$), Wehner³ was able to derive two possible sets of hyperfine parameters: (a) $\theta^H = 25.4 \pm 0.5^\circ$, $\phi^H = 0^\circ$, $\eta = 0.29 \pm 0.08$; (b) $\theta^H = 18.7 \pm 0.5^\circ$, $\phi^H = 90^\circ$, $\eta = 0.77 \pm 0.08$; and $\Delta E_Q(4.2$ K) = 3.37 ± 0.024 mm/sec, $H_{\text{int}}(4.2$ K) = 212 ± 3 kG.

The presence of a magnetic field \vec{H} reorients the spin states $|e_\alpha\rangle$ according to the interaction of the electron spin \vec{S} with \vec{H} . Depending on the magnitude of \vec{H} we therefore may get appreciable mixing between the zero-field states $|e_\alpha\rangle$, and thus the quadrupole splitting might be different from that in zero field. Figure 4 shows the field dependence of $\Delta E_Q(4.2$ K) from our calculations in which the electronic Hamiltonian contains also the inter-

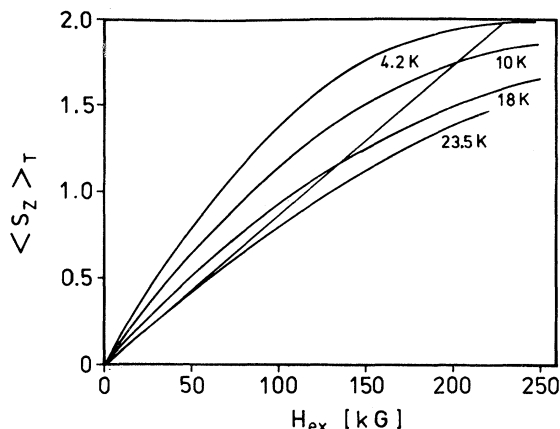


FIG. 5. Graphical solution for the spontaneous spin $\langle S_z \rangle_T$ in molecular-field approximation. The picture corresponds to case b of Fig. 2. (We get nearly exactly the same graphs for cases a and c.)

action $\mu_B(\hat{L} + 2\hat{S})\vec{H}$. In the molecular-field approximation for ferromagnetic or antiferromagnetic substances the exchange interaction is represented by an exchange field \vec{H}_{ex} .¹⁹ This field is proportional to the mean value of the spin, $\langle S_z \rangle_T$,²⁰⁻²²

$$H_{\text{ex}} = h \langle S_z \rangle_T,$$

where h is a constant. The particular value of the spin $\langle S_z \rangle_T$ is obtained by the self-consistency condition of molecular-field theory²⁰⁻²²: the spin $\langle S_z \rangle_T$ produced by the exchange field has to be equal to H_{ex}/h . The solution can be found graphically (Fig. 5). The intersections of the straight line and the $\langle S_z(H_{\text{ex}}) \rangle_T$ curves yield the self-consistent values of $\langle S_z \rangle_T$ for different temperatures T . The straight line is determined by the slope of $\langle S_z(H_{\text{ex}}) \rangle_T$ at $T = T_N$ and $H_{\text{ex}} = 0$,

$$\frac{d\langle S_z \rangle_T}{dH_{\text{ex}}} = h.$$

From Fig. 5 we find for $T = 4.2$ K,

$$\langle S_z \rangle_{4.2 \text{ K}} = 1.95; H_{\text{ex}} = 230 \text{ kG}.$$

Using this value of H_{ex} in Fig. 4, the magnetically induced quadrupole splitting ΔE_Q at 4.2 K takes the values 3.34, 3.38, and 3.39 mm/sec for the cases a, b, and c, respectively. This result is in reasonable agreement with the experimental low-temperature value $\Delta E_Q^{\text{exp}}(4.2$ K) = 3.37 ± 0.025 mm/sec. Moreover, we conclude from the calculated asymmetry parameter, $\eta = 0.2 \pm 0.05$, that we are concerned with Wehner's case (a).

We continue our investigation to derive from our calculations the orientation of \vec{H}_{int} relative to the main axis system of the EFG (θ^H , ϕ^H). The contribution of the spin dipolar term to the internal magnetic field, \vec{H}_{int} , should not be neglected, since this term may appreciably rotate the inter-

nal field off the spin direction. Since the energy splitting of the orbital states is fairly large compared to the nondiagonal elements of the spin-orbit coupling, the rotation of \vec{H}_{int} can be obtained by perturbation theory. Within this approximation, which is of the spin-Hamiltonian type,^{23,24} each component of the internal field is proportional to the spin average $\langle S_z \rangle$. Since the spin is parallel to the b ($=z$) axis we obtain,²⁰

$$\begin{aligned} H_{\text{int},z} &= [h^F - (g_z - 2)2\mu_B \langle \gamma_D^{-3} \rangle \\ &\quad - \frac{1}{7} \mu_B \langle \gamma_D^{-3} \rangle \langle l_z^2 - 2 \rangle] \langle S_z \rangle, \\ H_{\text{int},x} &= -\frac{1}{7} \mu_B \langle \gamma_D^{-3} \rangle \langle \frac{1}{2} (l_x l_z + l_z l_x) \rangle \langle S_z \rangle, \\ H_{\text{int},y} &= 0, \end{aligned}$$

where $h^F \langle S_z \rangle$ represents the Fermi-contact hyperfine field and the supertransferred hyperfine field, g_z is the z component of the g tensor, and μ_B the Bohr magneton. For $\langle S_z \rangle = \pm 2$ (corresponding to our spin ground state for $H_{\text{ex}} = 230$ kG) the rotation of the internal field results in

$$\theta^{\text{int}} = \arcsin \frac{-\frac{2}{7} \mu_B \langle \gamma_D^{-3} \rangle \langle \frac{1}{2} (l_x l_z + l_z l_x) \rangle}{212 \text{ kG}}$$

and

$$\phi^{\text{int}} = 0,$$

where the total internal field has been taken as 212 kG, and the Fermi-contact part of the internal magnetic field is assumed larger than the part arising from the orbital angular momentum and the

spin dipolar term. With the free-ion value²⁵

$$\frac{1}{7} \mu_B \langle \gamma_D^{-3} \rangle = 40 \text{ kG},$$

which may be corrected by a reduction factor 0.9 to get the effective value of $\frac{1}{7} \mu_B \langle \gamma_D^{-3} \rangle \approx 36$ kG, and with $\frac{1}{2} \langle l_x l_z + l_z l_x \rangle = -0.6$ from our MO calculations, we find

$$\theta^{\text{int}} = 11.7^\circ.$$

Since the main axis V_{zz} is rotated by an angle $\theta = -16^\circ$, the polar angles of \vec{H}_{int} relative to the main axis system of the EFG lead to

$$\theta^H = 27.7^\circ \quad \text{and} \quad \phi^H = 0,$$

which again supports case (a).

We finally conclude that our theoretical study of the electronic and magnetic structure of α -FeSO₄ is in agreement with the recent experimental findings of Wehner.³ Summarizing our results we find $\Delta E_Q^{\text{calc}}(T)$ and $\chi^{\text{calc}}(T)$ in agreement with experiment in the paramagnetic region; and for $T = 4.2$ K the EFG component V_{zz} and \vec{H}_{int} relative to the crystallographic frame ($x=c$, $y=a$, $z=b$) are specified by $\Delta E_Q(4.2 \text{ K}) = 3.37 \pm 0.05$ mm/sec, $\eta = 0.20 \pm 0.05$, $\theta = -16^\circ$, $\phi = 0^\circ$, and $H_{\text{int}}(4.2 \text{ K}) = 212$ kG, $\theta^H = 11.7^\circ$, $\phi^H = 0^\circ$.

ACKNOWLEDGMENTS

We wish to thank Dr. S. K. Date and Dr. H. Wehner for many helpful discussions.

*Supported in part by the Deutsche Forschungsgemeinschaft and in part at the University of Utah by the NSF Grant No. MPS75-01284.

¹K. Ono and A. Ito, J. Phys. Soc. Jpn. **19**, 899 (1964).

²Hang Nam Ok, Phys. Rev. B **4**, 3870 (1971).

³H. Wehner, thesis (Universität Erlangen-Nürnberg, BRD, 1973) (unpublished).

⁴A. S. Borovik-Romanov, V. R. Karasik, and N. M. Kreines, Zh. Eksp. Teor. Fiz. **31**, 18 (1956) [Sov. Phys. -JETP **4**, 109 (1957)].

⁵D. Samaras and J. Coing-Boyat, Bull. Soc. Fr. Mineral. Cristallogr. **93**, 190 (1970).

⁶B. C. Frazer and P. J. Brown, Phys. Rev. **125**, 1283 (1962).

⁷A. Trautwein and F. E. Harris, Theor. Chim. Acta **30**, 45 (1973).

⁸C. J. Ballhausen, *Introduction to Ligand Field Theory*, (McGraw-Hill, New York, 1962).

⁹S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York 1970).

¹⁰J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge U.P., Cambridge, England, 1964).

¹¹A. A. Missetich and T. Buch, J. Chem. Phys. **41**, 2524 (1964).

¹²R. E. Trees, Phys. Rev. **82**, 683 (1951).

¹³A. A. Missetich and R. E. Watson, Phys. Rev. **143**, 335 (1966).

¹⁴R. M. Sternheimer, Phys. Rev. **92**, 1460 (1953).

¹⁵R. Ingalls, Phys. Rev. **128**, 1155 (1962); R. M. Sternheimer, Phys. Rev. **130**, 1423 (1963).

¹⁶B. Bleaney, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic, New York, 1967).

¹⁷M. Weissbluth and J. E. Maling, J. Chem. Phys. **47**, 4166 (1967).

¹⁸J. L. K. F. de Vries, C. P. Kreijzers, and F. DeBoer, Inorg. Chem. **11**, 1343 (1972); A. Trautwein and F. E. Harris, Phys. Rev. B **7**, 4755 (1973).

¹⁹For an exchange interaction $J \vec{S}_i \cdot \vec{S}_j$ between different ions i and j , the exchange field acts only on \vec{S} and not on \vec{L} . In the present case the matrices of \vec{L} and \vec{S} within the basis of the five ground states are approximately proportional. Thus, without changing the general theory, H_{ex} may act on the magnetic moment.

²⁰P. Weis, J. Phys. **6**, 667 (1907).

²¹C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York, 1966).

²²G. R. Davidson, M. Eibschütz, and H. J. Guggenheim, Phys. Rev. B **8**, 1864 (1973).

²³M. H. L. Pryce, Proc. Phys. Soc. Lond. A **63**, 25 (1950).

²⁴R. Zimmermann, H. Spiering, and G. Ritter, Chem. Phys. **4**, 133 (1974).

²⁵A. J. Freeman and R. E. Watson, Phys. Rev. **131**, 2566 (1963).