

Magnetic Anisotropy and Electronic Structure of Gillespite, a Mineral containing Planar, Four-co-ordinate, High-spin Iron(II)

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The single-crystal magnetic anisotropy of gillespite, a rare mineral containing Fe^{II} in a square-planar ligand geometry, is reported over the range 4.2—298 K. Good agreement is obtained between the calculated and observed magnetic parameters using a crystal-field model assuming a ⁵A_{1g} ground state and with excited state energies compatible with the electronic spectrum. However, the value of the orbital-reduction parameter *k* is considerably lower than expected. An analysis of the *d*-orbital energies in gillespite and the isomorphous copper analogue egyptian blue using the angular-overlap model is presented. This suggests the presence of an abnormally strong π-bonding interaction, although more reasonable ligand-bonding parameters are obtained if it is assumed that the a_{1g}(d_{z²}) orbital is depressed in energy by ca. 5 000 cm⁻¹ by configuration interaction with the a_{1g}(4s) orbital in these compounds. It is shown that the electronic spectrum of the high-pressure form of gillespite is consistent with a flattened tetrahedral ligand geometry about the Fe^{II}, but it is proposed that the distortion from planarity is probably considerably greater than that suggested as a result of a previous X-ray crystal-structure determination.

THE rare mineral gillespite, BaFeSi₄O₁₀, is unusual in that it contains Fe^{II} in a planar four-co-ordinate ligand environment.^{1,2} On the basis of the polarized electronic spectrum Burns *et al.*³ suggested a spin-quintet ground state for the compound, with the iron(II) *d*-orbital sequence $d_{x^2-y^2} \gg d_{xy} > d_{xz, yz} > d_{z^2}$. Gillespite has a distinctive Mössbauer spectrum⁴ and is also anomalous in that it undergoes a reversible colour change at 26 kbar.^{5,†} This latter property was originally thought to be associated with a spin change,⁵ but has since been shown to be due to a phase transition designated gillespite(I) → gillespite(II) in which the ligand co-ordination around the Fe^{II} changes to a highly flattened tetrahedral geometry.^{2,6}

While the magnetic properties of planar iron(II) complexes with spin-triplet ground states have been quite well characterized,^{7,8} virtually no information has been available on high-spin complexes of this kind. The purpose of the present study has therefore been to investigate the single-crystal magnetic properties of gillespite(I) and to attempt to rationalize these in terms of the energy levels of this compound. The nature of the metal-ligand bonding in this and similar compounds is discussed using the simple molecular-orbital angular-overlap model of Jørgensen and Schäffer.⁹

EXPERIMENTAL

It is difficult to obtain accurate measurements of the magnetic susceptibility of gillespite since both the crystal properties and magnetic properties are extremely anisotropic. The crystals cleave very readily in the (001) plane and even after grinding the crystallites are in the form of small plates which tend to pack in an ordered manner. The magnetic anisotropy is also very large and even a slight tendency toward non-uniform packing can lead to large discrepancies when one attempts to measure the average magnetic susceptibility. The large magnetic anisotropy also causes the crystallites to align themselves in the applied

magnetic field, particularly at the magnetic field strength used (1—5 T). These two tendencies for the crystals to be non-randomly orientated may reinforce or oppose each other depending on the method used for packing the sample holder and also on the orientation of the applied magnetic field with respect to the balance system used for measuring the resultant force.

These problems were overcome by measuring the susceptibility of finely ground gillespite in a petroleum jelly (vaseline) mull. The masses of vaseline and gillespite were subsequently determined by the Australian National University Microanalytical Service and the results corrected for the diamagnetism of the vaseline. The latter correction was found to be quite small and independent of temperature down to 4.2 K. The tendency of the crystallites to align in the magnetic field was so large that at room temperature in a field of 4T the vaseline was not viscous enough to prevent partial alignment from occurring. The average magnetic moment was thus only determined up to 278 K although it remained constant at 5.01 B.M. at >50 K. The room-temperature value was therefore assumed to be 5.01 B.M. which is significantly different from the literature value of 5.12 B.M.³

Gillespite occurs as small inclusions in a matrix consisting primarily of sanbornite BaSi₂O₅.¹ The latter mineral is colourless, cleaves in a similar manner to gillespite, and is difficult to separate from it. There is also a dark impurity inside most of the lumps of gillespite and pure samples of gillespite were obtained by rough grinding of the crude mineral and mechanical separation of the BaFeSi₄O₁₀ under a microscope. The anisotropy was measured on a small crystal weighing 1.405 mg.

We were unable to measure $\chi_{||}$ directly since the large anisotropy caused the crystal to be dragged to the side of the insert in the Dewar. Moreover, $\chi_{||}$ is quite small, particularly at low temperatures, and would be subject to larger errors for very small deviations from correct alignment. It was possible to measure χ_{\perp} directly and the results were in excellent agreement with the values derived from $\bar{\chi}$ and $\Delta\chi$ (see Figure 2). The measurements of χ_{\perp} were confined to temperatures ca. <20 K since at higher temperatures the diamagnetic correction due to the sample holder became significant.¹⁰ The internal consistency of the low-

† Throughout this paper: 1 bar = 10⁵ Pa; 1 B.M. ≈ 9.27 × 10⁻²⁴ A m².

temperature values of χ_{\perp} , $\Delta\chi$, and $\bar{\chi}$ is taken as evidence for the reliability of our measurements of $\bar{\chi}$.

The average susceptibility was measured by the Faraday method and the magnetic anisotropy was measured by the Krishnan critical-torque method using equipment described previously.¹¹ The crystal-field and magnetization calculations were performed using computer programs described elsewhere.¹²⁻¹⁴

RESULTS AND DISCUSSION

Magnetic Properties.—The crystallographic site symmetry of the Fe^{2+} ion in gillespite(I) is C_4 and in this symmetry only orbital singlets and doublets are allowed. If the ground state is a spin triplet then the maximum magnetic moment that could occur is that of a 3E state with no orbital quenching. This would be far less than the observed room-temperature magnetic moment and hence the ground state must be either a spin quintet or else a spin triplet with a spin-quintet state that is appreciably populated at room temperature. The latter possibility seems unlikely since the average magnetic moment is independent of temperature down to *ca.* 50 K. The ground state would therefore appear to be a spin quintet while the closeness of the room-temperature magnetic moment to the spin-only value (4.90 B.M.) suggests that it is an orbital singlet. Calculations involving all the triplet levels confirm this assumption (see later) and preliminary calculations can be restricted to the 25 states arising from the 5D free-ion state.

Although its strict site symmetry is C_4 , the Fe^{2+} ion is only 0.03 Å out of the plane of the four co-ordinating oxygen atoms (O-Fe-O 178°) and the microsymmetry is very close to D_{4h} . The effect of lower symmetry is discussed later but for the moment we will assume D_{4h} symmetry as has been proposed by previous workers.^{3,4} The crystal field is parametrized in terms of the single-electron orbital energies transforming as $a_{1g}(z^2)$, $b_{1g}(x^2 - y^2)$, $b_{2g}(xy)$, and $e_g(xz, yz)$. The visible spectrum of gillespite has been assigned³ on the basis of a ${}^5A_{1g}$ ground state with ${}^5B_{2g}$ at 8 300 cm^{-1} and ${}^5B_{1g}$ at 20 000 cm^{-1} . The 5E_g state was not observed and was presumed to lie between 500 and 1 500 cm^{-1} . A later paper¹⁵ comparing the electronic spectrum of gillespite and the isomorphous copper compound suggested an energy separation of the ${}^5A_{1g}$ and 5E_g levels of gillespite of *ca.* 2 850 cm^{-1} .

If this assignment is correct the principal magnetic moments should depend only on the spin-orbit coupling constant (ζ), the orbital-reduction factor (k), and the energy of the 5E_g level (ΔE). The interpolated experimental values of $\bar{\mu}$ and $\Delta\chi$ are given in Tables 1 and 2.

The calculated values of μ_{\parallel} were found to be almost completely independent of k but were quite strongly dependent on ζ and ΔE , particularly at low temperatures. The value of μ_{\parallel} decreased with decreasing ΔE and increasing ζ . The reverse behaviour was found for μ_{\perp} . Assuming ζ to be no greater than the free-ion value of 400 cm^{-1} , it was possible to obtain a reasonable fit (standard deviation <0.1 B.M.) to μ_{\parallel} for ζ and ΔE

values ranging linearly from $\zeta = 400 \text{ cm}^{-1}$, $\Delta E = 1\ 925 \text{ cm}^{-1}$ to $\zeta = 200 \text{ cm}^{-1}$, $\Delta E = 375 \text{ cm}^{-1}$. For lower values

TABLE 1
Comparison of interpolated and calculated values of $\bar{\mu}$

T/K	expt.	$\bar{\mu}/\text{B.M.}$		
		Calc.		
		Set 1	Set 2	Set 3
300	5.01	5.04	5.02	5.05
250	5.01	5.04	5.02	5.03
200	5.01	5.04	5.02	5.03
150	5.01	5.03	5.02	5.02
100	5.01	5.02	5.02	5.01
80	5.01	5.02	5.02	5.01
60	5.01	5.01	5.01	4.99
50	5.00	4.99	4.99	4.98
40	4.95	4.97	4.97	4.95
30	4.92	4.93	4.93	4.91
25	4.86	4.89	4.89	4.87
20	4.79	4.83	4.83	4.81
15	4.68	4.72	4.72	4.70
10	4.46	4.51	4.50	4.48
8	4.27	4.34	4.32	4.30
6.5	4.06	4.14	4.11	4.09
5	3.78	3.81	3.78	3.75
4.17	3.52	3.55	3.51	3.49

TABLE 2
Comparison of interpolated and calculated values of $10^6(\chi_{\perp} - \chi_{\parallel})/\text{cm}^3 \text{ mol}^{-1}$

T/K	expt.	Calc.		
		Set 1	Set 2	Set 3
300	2 740	2 290	2 230	2 260
250	3 400	3 010	2 950	2 950
200	4 740	4 250	4 190	4 200
150	7 160	6 740	6 670	6 680
100	13 900	13 100	13 100	13 100
80	20 300	19 100	19 100	19 000
60	31 500	30 700	30 700	30 700
50	42 200	41 300	41 300	41 300
40	58 800	58 800	58 700	58 700
30	89 000	90 000	90 100	89 800
25	112 000	116 000	116 000	115 000
20	149 000	154 000	154 000	153 000
15	207 000	214 000	214 000	212 000
10	314 000	319 000	320 000	315 000
8	394 000	384 000	387 000	381 000
6.5	472 000	445 000	448 000	439 000
4.58	550 000	527 000	533 000	517 000

of ζ (and hence ΔE) the fit to μ_{\parallel} deteriorated due to thermal population of the 5E_g level. The best fit was obtained by using $\zeta = 300 \text{ cm}^{-1}$ and $\Delta E = 1\ 150 \text{ cm}^{-1}$. The value of μ_{\perp} was found to decrease with decreasing k , and using the same values of ζ and ΔE the best fit to μ_{\perp} was found for $k = 0.25$. Between 20 and 300 K the standard deviations to the fits to μ_{\parallel} and μ_{\perp} were 0.06 and 0.02 B.M. respectively. The fit could not be improved significantly by systematic variation of the three parameters around these values. This set of parameters (set 1) is listed in Table 4 and the calculated and experimental values of $\bar{\mu}$ and $\Delta\chi$ are compared in Tables 1 and 2. The calculated and experimental values of μ_{\perp} and μ_{\parallel} are shown in Figure 1.

Using parameter set 1, g_{\parallel} and g_{\perp} for the ${}^5A_{1g}$ manifold were calculated to be 1.979 and 2.082 respectively. For $k = 1.0$ and all the other parameters the same, g_{\parallel} and g_{\perp} would be 1.989 and 2.343 respectively. The reason

that k has little effect on μ_{\parallel} is now apparent since g_{\parallel} is only slightly removed from the spin-only value and there is little orbital angular momentum mixed into the ${}^5A_{1g}$ ground state by the spin-orbit operator $\hat{L}_z\hat{S}_z$. For the range of values of ζ to ΔE mentioned previously the zero-field splitting of the ${}^5A_{1g}$ state was found to be almost constant. The same was true of the calculated g values for small values of k .

At low temperatures, the second-order Zeeman contribution to the magnetic susceptibility should be negligible and if no other states are thermally accessible the magnetism should be dominated by the ${}^5A_{1g}$ manifold. In this case, the principal magnetic moments and their

$$\mathcal{H} = \beta(H \cdot g \cdot S) + B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 \quad (1)$$

field dependence can be calculated using the spin Hamiltonian (1). The eigenvalues of the operators

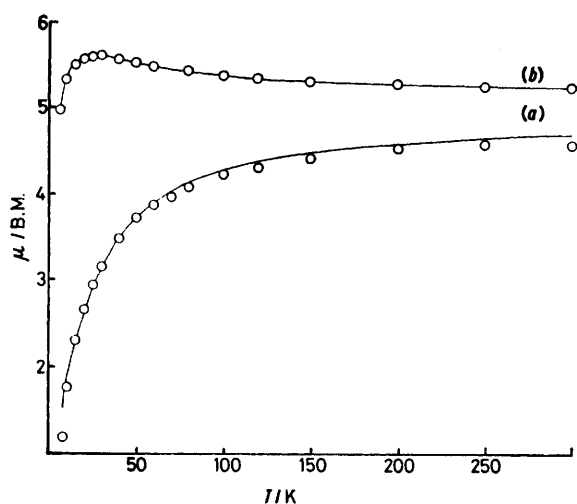


FIGURE 1 Interpolated experimental values of μ_{\parallel} (a) and μ_{\perp} (b). The curves are calculated using parameter set 1. The values calculated using parameter sets 2 and 3 are the same within 0.02 B.M.

O_L^M are given by Abragam and Bleaney.¹⁶ In the absence of fourth-order terms a quintet state is split into three levels transforming in the same way as the wavefunctions $|0\rangle$, $|\pm 1\rangle$, and $|\pm 2\rangle$ at relative energies of 0, $3 B_2^0$, and $12 B_2^0$ respectively. The inclusion of the B_4^0 term causes the relative energies of the $|\pm 2\rangle$ and $|\pm 1\rangle$ states to deviate from the ratio 4 : 1 while the B_4^4 is responsible for the very small splitting of the $|\pm 2\rangle$ states. Using parameter set 1 and assuming no splitting of the $|\pm 2\rangle$ states it is possible to calculate the value of g_{\parallel} within this doublet. For a pure ${}^5A_{1g}$ manifold the value should be exactly twice that of the $|\pm 1\rangle$ states and in the present case the ratio is found to be 2.004 : 1 indicating again that little orbital angular momentum is mixed into the ${}^5A_{1g}$ manifold by the spin-orbit operator $\hat{L}_z\hat{S}_z$. The small splitting of the $|\pm 2\rangle$ states has a negligible effect on the magnetic susceptibility at low temperatures since they are not appreciably occupied and are only mixed into the $|0\rangle$ state in second

order in the magnetic field. The usual zero-field splitting parameter D is equal to $3B_2^0$ and the splittings calculated from the crystal-field model can be reproduced for $D = 11.86 \text{ cm}^{-1}$ and $B_4^0 = 0.0036 \text{ cm}^{-1}$. The Raman spectrum of gillespite was measured, and found to show a sharp peak at a shift of 10.8 cm^{-1} on excitation with the 488.0-nm line of the argon laser. While this could be due to the transition from the $|0\rangle$ to the $|\pm 1\rangle$ spin states, the peak was absent on excitation with the 514.5- and 457.9-nm laser lines, so that it is possible that it has some other origin such as phosphorescence. The spin-Hamiltonian parameters are given in Table 3 and hence-

TABLE 3

Magnetic parameters calculated for gillespite(1)

k	T/K	Including second-order Zeeman effect		Neglecting second-order Zeeman effect	
		$\bar{\mu}$	$\Delta\chi/\text{cm}^3 \text{ mol}^{-1}$	$\bar{\mu}$	$\Delta\chi/\text{cm}^3 \text{ mol}^{-1}$
1.0	300	5.67	6 300	5.46	5 000
	100	5.55	23 400	5.48	22 100
	50	5.51	617 000	5.48	60 500
	10	5.01	407 000	5.00	40 800
0.25	300	5.05	2 260	5.01	2 190
	100	5.01	13 100	5.00	13 100
	50	4.98	41 300	4.97	41 400
	10	4.48	315 000	4.48	317 000
0.0	300	4.89	1 310	4.86	1 330
	100	4.85	10 200	4.85	10 300
	50	4.81	35 300	4.81	35 500
	10	4.31	288 000	4.31	289 000

forth will be called parameter set 2. The agreement between the experimental values of μ_{\perp} and those calculated from the spin Hamiltonian is excellent as can be seen from Figure 2. As mentioned previously, χ_{\parallel} could not be measured directly and μ_{\parallel} had to be calculated from $\bar{\chi}$ and $\Delta\chi$. The discrepancy between calculated and experimental values of μ_{\parallel} at $<10 \text{ K}$ may be due to the fact that χ_{\parallel} is obtained as a small difference between two large numbers ($\bar{\chi}$ and $\Delta\chi$) and the relative error becomes quite significant. At low temperatures the magnetic susceptibility is due primarily to a second-order Zeeman mixing of the $|0\rangle$ and $|\pm 1\rangle$ states and hence as $T \rightarrow 0$, $\mu_{\parallel} \rightarrow 0$ and $\chi_{\perp} \rightarrow \text{constant}$. The variation of μ , with magnetic field strength is shown in Figure 3 and again there is good agreement between calculated and experimental values. The overall fit could not be significantly improved by treating g_{\parallel} , g_{\perp} , D , and B_4^0 as freely adjustable parameters.

Although the low-temperature magnetism should be dominated by the ${}^5A_{1g}$ manifold, this is not necessarily so at higher temperatures since the ${}^5A_{1g} - {}^5E_g$ separation is only ca. 1100 cm^{-1} . The 5E_g level can be mixed into the ${}^5A_{1g}$ level by the magnetic field and hence there should be a significant second-order Zeeman contribution to the magnetic moment as well as a small first-order Zeeman contribution due to thermal population of the 5E_g level. However, it is seen from Tables 1 and 2 that the spin Hamiltonian reproduces both μ_{\parallel} and μ_{\perp} (and hence $\bar{\mu}$ and $\Delta\chi$) even up to room temperature. The reason for this can be seen from Table 3 where the values of $\bar{\mu}$ and $\Delta\chi$

calculated from the crystal-field model are shown with and without the inclusion of the second-order Zeeman

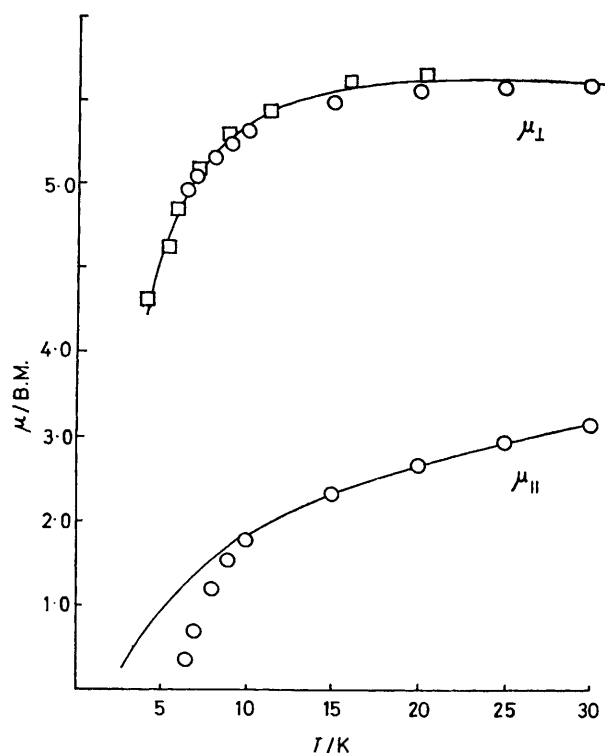


FIGURE 2 Low-temperature principal magnetic moments of gillespite: (O), determined from the values of the magnetic anisotropy and $\bar{\chi}(1\text{ T})$; (□) measured directly at a field strength of 1 T. The curves were calculated using parameter set 2

contribution. At low temperatures, as expected, the difference is insignificant but at high temperatures the second-order Zeeman contribution is important only when k is close to unity. The magnetic field mixes predominantly orbital angular momentum into the ground-state manifold and for small values of k this has a correspondingly small effect on the calculated magnetic susceptibility.

The low value of k is surprising and, since the value obtained can depend on the size of the basis set used in the calculations,¹⁷ some calculations were performed using an enlarged basis set. For the d^6 configuration the inclusion of spin-triplet terms greatly increases the complexity of the calculations since the basis set increases from 25 to 160 wavefunctions. It was not considered worthwhile to include a restricted number of spin-triplet levels since there are expected to be a large number of low-lying states arising from different free-ion terms. Moreover, the states could be strongly admixed by the crystal field and spin-orbit coupling as has been shown to occur in the d^8 configuration.¹⁸

No spin-forbidden bands have been assigned in the spectrum of gillespite and hence the interelectron-repulsion parameters F_2 and F_4 were assumed to be 1 000 and 80 cm^{-1} respectively. The inclusion of all the spin-triplet levels did not have a very large effect on the

calculated magnetic susceptibilities. The value of μ_{\parallel} was still found to be almost completely independent of k and showed the same linear dependence on ΔE and ζ although slightly smaller values of both were favoured. The best fit to both μ_{\parallel} and μ_{\perp} was obtained for $\zeta = 250$ cm^{-1} , $\Delta E = 1\,000$ cm^{-1} , and $k = 0.25$. The magnetic properties calculated using these parameters (set 3) are virtually identical to those obtained previously as can be seen in Tables 1 and 2. It seems that the low value of k is not due to the use of a restricted basis set. However, covalency effects alone cannot explain such a significant quenching of the orbital angular momentum. It is possible that a dynamic Jahn-Teller effect occurs in the 5E_g excited state, and that this causes the effective lowering of k . It is unfortunate that as yet no other examples of planar high-spin iron(II) complexes are available for comparison.

For obvious reasons it was not possible to carry out an exhaustive investigation of the magnetism within the extended basis set of quintet and triplet free-ion terms. However, it was found that for $\zeta = 400$ or 250 cm^{-1} , $F_2 = 1\,000$ cm^{-1} , $F_4 = 80$ cm^{-1} , and ${}^5B_{1g} = 19\,000$ cm^{-1} it was not possible to fit the magnetic properties to any ground state other than ${}^5A_{1g}$, nor was it possible to interchange the 5E_g and ${}^5B_{2g}$ levels. It thus seems clear that the previous interpretation of the electronic spectrum of gillespite³ is correct. The various parameters used to calculate the magnetic properties are summarized in Table 4.

Metal-Ligand Bonding Parameters.—The electronic spectrum of gillespite, supported by the magnetic properties, suggests the energies $E(x^2 - y^2) = 20\,000$ and $E(xy) = 8\,300$ cm^{-1} relative to $E(z^2)$ set arbitrarily to 0. Although $E(xz, yz)$ cannot be determined directly, comparison with the analogous copper(II) complex, and consistency with the magnetic data, suggests a value $E(xz, yz) = 2\,000 \pm 1\,000$ cm^{-1} . Perhaps the best method of rationalizing d -orbital energies in terms of the metal-ligand bonding is the angular-overlap model (a.o.m.) developed by Jørgensen and Schäffer.⁹ This

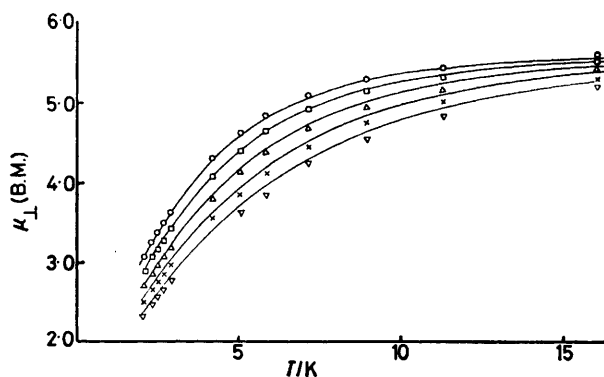


FIGURE 3 Values of μ_{\perp} at low temperatures on magnetic fields of 1 (O), 2 (□), 3 (Δ), 4 (×), and 5 T (▽). The curves were calculated using parameter set 2

relates the energy e by which a d orbital is raised on interaction with a ligand orbital to the square of the diatomic

overlap integral S via equation (2). Here H_L and H_M are the diagonal matrix elements of the ligand and metal

$$e = S^2 K \quad (2a)$$

$$K = H_L^2 / (H_M - H_L) \quad (2b)$$

orbitals, respectively. Both σ and π interactions may be included, and the total energy of each d orbital E is

TABLE 4

Summary of parameters used in calculating the magnetism of gillespite(I). Except for the g values, all units are cm^{-1}

	Set 1 ^a	Set 2	Set 3 ^b
F_2			1 000
F_4			80
ζ	300		250
$E(z^2)^c$	0		0
$E(xz, yz)$	1 150		1 000
$E(xy)^c$	7 500		7 500
$E(x^2 - y^2)^c$	19 000		19 000
k	0.25		0.25
g_{\parallel}	1.979 ^d	1.979	1.976 ^d
g_{\perp}	2.082 ^d	2.082	2.077 ^d
$E(1)^e$	11.42	11.42	11.80
$E(2)^f$	47.19,	47.21	48.09,
	47.26		48.63
$D(=3B_2^0)$		11.86	
B_4^0		0.003 6	

^a Basis set ⁵D. ^b Basis set ⁵D, ³P1, ³P2, ³D, ³F1, ³F2, ³G, ³H. ^c Values from electronic spectra, reduced slightly in energy to take into account vibrational effects (see ref. 15). ^d Calculated from the crystal-field parameters. ^e Calculated energy of the $|\pm 1\rangle$ state relative to the $|0\rangle$ ground state. ^f Calculated energy of the $|\pm 2\rangle$ state relative to the $|0\rangle$ ground state.

obtained by summing over all the ligands and ligand orbitals using the angular-overlap matrix appropriate to the geometry of the complex in question.

The ligand-field symmetry in gillespite(I), considering just the Fe^{II} and four oxygen ligand atoms, is C_{4v} , and the metal-ligand interaction may be parametrized using the three parameters $e_{\sigma}, e_{\pi}(a)$, and $e_{\pi}(e)$ where the symbols a and e denote that the ligand π orbitals are parallel or perpendicular to the symmetry axis, respectively. The d -orbital energies are given by equation (3) where θ is the

$$E(x^2 - y^2) = 0.75(1 - \cos\theta)^2 e_{\sigma} + \sin^2\theta e_{\pi}(a) \quad (3a)$$

$$E(z^2) = 4[0.25 + 0.75\cos\theta]^2 e_{\sigma} + 0.75\sin^2\theta e_{\pi}(a) \quad (3b)$$

$$E(xy) = 4\sin^2(\theta/2) e_{\pi}(e) \quad (3c)$$

$$E(xz, yz) = 2\{[\cos(\theta/2)^2 + \cos^2\theta] e_{\pi}(a) + 0.75\sin^2\theta e_{\sigma}\} \quad (3d)$$

angle O-Fe-O involving the *trans* oxygen atoms.¹⁹ In gillespite(I) this is 178° , and substitution of the appropriate d -orbital energies in the above equations yields the parameters $e_{\sigma} = 10\,000\text{ cm}^{-1}$, $e_{\pi}(a) = 6\,000 \pm 500\text{ cm}^{-1}$, and $e_{\pi}(e) = 4\,575\text{ cm}^{-1}$. Substitution of the diatomic overlap integrals $S_{\sigma} = 0.114\,11$ and $S_{\pi} = 0.069\,42$ estimated for $\text{Fe}^+ 3d$ and oxygen $2p$ orbitals* at 1.995

* Calculated using the 'double-zeta' functions of J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. E. Edgell (*J. Chem. Phys.*, 1962, **36**, 1057) for the $3d$ functions of Fe^+ and Cu^+ and those of E. Clementi ('Tables of Atomic Functions,' I.B.M. Research Report, 1965) for the oxygen $2p$ function.

\AA^2 into equation (2b) gives ligand-bonding parameters $K_{\sigma} = 7.68 \times 10^6\text{ cm}^{-1}$, $K_{\pi}(a) = (12.45 \pm 1.0) \times 10^6\text{ cm}^{-1}$, and $K_{\pi}(e) = 9.49 \times 10^6\text{ cm}^{-1}$ for the silicate oxygen atoms towards Fe^{II} [the uncertainty in $K_{\pi}(a)$ and $e_{\pi}(a)$ arising from the uncertainty in $E(xz, yz)$].

It is of interest to compare these parameters with those estimated for the isomorphous copper(II) analogue 'egyptian blue.' The electron spectrum of this compound consists of peaks centred at $12\,900$, $15\,800$, and $18\,800\text{ cm}^{-1}$,^{15,20} and these have been assigned¹⁵ to the transitions ${}^2B_{2g}(xy) \rightarrow {}^2B_{1g}(x^2 - y^2)$, ${}^2E_g(xz, yz) \rightarrow {}^2B_{1g}(x^2 - y^2)$, and ${}^2A_{1g}(z^2) \rightarrow {}^2B_{1g}(x^2 - y^2)$, respectively. Equations (3a)–(3d) yields the parameters $e_{\sigma} = 9\,400\text{ cm}^{-1}$, $e_{\pi}(a) = 6\,200\text{ cm}^{-1}$, and $e_{\pi}(e) = 4\,575\text{ cm}^{-1}$, while substitution of the overlap integrals $S_{\sigma} = 0.093\,78$ and $S_{\pi} = 0.054\,27$ appropriate to the Cu-O bond length²¹ of 1.91 \AA yields the ligand-bonding parameters $K_{\sigma} = 10.69 \times 10^6\text{ cm}^{-1}$, $K_{\pi}(a) = 21.05 \times 10^6\text{ cm}^{-1}$, and $K_{\pi}(e) = 15.53 \times 10^6\text{ cm}^{-1}$ for the silicate oxygen atoms towards Cu^{II} . It may be noted that the parameters e_{σ} , *etc.* represent a metal-ligand interaction in a particular compound, while K_{σ} , *etc.* are constants for the ligand and metal under consideration which, within the framework of the model, should be independent of metal-ligand distance and the geometry of the complex. The similarity between the two complexes for the values of $e_{\sigma}, e_{\pi}(a)$, and $e_{\pi}(e)$ suggests an analogous ordering of the d -orbital energies. Although the sequence $K_{\pi}(a) > K_{\pi}(e) > K_{\sigma}$ is identical for both compounds, the ligand-bonding parameters of the copper complex are significantly larger than those of gillespite. This is in agreement with simple theory, since the factor $H_M - H_L$ in equation (2b) should be larger for Fe^{II} than Cu^{II} because of the greater effective nuclear charge of the latter metal ion. A similar change in K was observed in a comparison of nickel(II) and copper(II) pentane-2,4-dionato-complexes.²² The most surprising feature of the analysis of the d -orbital energies is the high value of the π -bonding parameters. In complexes with spherically symmetrical ions, *e.g.* Cl^- or O^{2-} , the a.o.m. in its simple form predicts that the antibonding interaction should depend just on S^2 , *i.e.* $K_{\sigma} = K_{\pi}(a) = K_{\pi}(e)$. Since $S_{\sigma} \approx 2S_{\pi}$, it is expected that $e_{\sigma} \approx 4e_{\pi}$ and available experimental evidence tends to support this. In the present complexes K_{π} is much larger than K_{σ} , and the π interactions $e_{\pi}(a)$ are over half as large as the σ interactions e_{σ} . The situation in gillespite and egyptian blue is complicated by the fact that the oxygen ligands are also co-ordinated to silicon so that the initial degeneracy of the σ and π orbitals is destroyed. However, in other compounds this would seem to have no drastic effect on the relative magnitudes of K_{σ} and K_{π} .^{23,†}

A possible explanation of the anomalous a.o.m. parameters in the present compounds is provided by a

† For instance, the values $K_{\sigma} = (8.6 \pm 0.4) \times 10^5\text{ cm}^{-1}$, $K_{\pi}(a) = (10.6 \pm 2.0) \times 10^5\text{ cm}^{-1}$, and $K_{\pi}(e) = (11.2 \pm 2) \times 10^5\text{ cm}^{-1}$ were recently determined for the water molecule towards Cu^{2+} in a series of hexa-aquacopper(II) complexes (M. A. Hitchman and T. D. Waite, *Inorg. Chem.*, 1976, **15**, 2150).

number of recent studies which suggest that the simple form of the a.o.m. is inadequate to describe the energies of the d orbitals in planar metal complexes.²⁴⁻²⁷ The failure arises because of the mixing of the metal $a_{1g}(4s)$ orbital into the $a_{1g}(3d_{z^2})$ orbital which occurs in a complex of D_{4h} symmetry. The extent of this admixture is proportional to the difference in metal-ligand overlap along the z and (xy) axes, and because of the diffuse nature of the $4s$ orbital this is significant only when axial ligation is completely absent,²⁴ as is the case in gillespite and egyptian blue. In a recent study of chlorocuprate(II) complexes with a wide variety of stereochemistries,²⁵ it was found that the d -orbital energies could be adequately described using a single angular-overlap parameter K , except for the planar $[\text{CuCl}_4]^{2-}$ ion in which the d_{z^2} orbital was found to be depressed in energy by *ca.* 5 000 cm^{-1} from the value predicted using the a.o.m. in its simple form. Similarly, in planar nickel(II) diamine complexes, which provide a particularly useful test of bonding models since covalent π interactions are absent, it has been found²⁶ that the electronic spectra can only be understood if the d_{z^2} orbital is depressed in energy by *ca.* 6 000 cm^{-1} from the value predicted by the simple bonding model. Direct confirmation of an admixture of the metal $4s$ orbital with the $3d_{z^2}$ orbital has also recently been provided from the isotropic hyperfine coupling constants of planar cobalt(II) complexes with ${}^2A_1(d_{z^2})$ ground states.²⁷ If a lowering in energy of the $a_{1g}(d_{z^2})$ orbital of 5 000 cm^{-1} is also assumed to occur in gillespite and egyptian blue, substitution of the corrected d -orbital energies in equations (2) and (3) yields the parameters $e_\sigma = 7\,500\text{ cm}^{-1}$, $e_\pi(a) = 2\,250 \pm 500\text{ cm}^{-1}$, $e_\pi(e) = 2\,700\text{ cm}^{-1}$, $K_\sigma = 5.76 \times 10^5\text{ cm}^{-1}$, $K_\pi(a) = (4.67 \pm 1.0) \times 10^5\text{ cm}^{-1}$, and $K_\pi(e) = 5.60 \times 10^5\text{ cm}^{-1}$ for $\text{BaFeSi}_4\text{O}_{10}$, and $e_\sigma = 6\,900\text{ cm}^{-1}$, $e_\pi(a) = 2\,450\text{ cm}^{-1}$, $e_\pi(e) = 1.950\text{ cm}^{-1}$, $K_\sigma = 7.96 \times 10^5\text{ cm}^{-1}$, $K_\pi(a) = 9.85 \times 10^5\text{ cm}^{-1}$, and $K_\pi(e) = 6.80 \times 10^5\text{ cm}^{-1}$ for $\text{BaCuSi}_4\text{O}_{10}$. These parameters seem quite reasonable, both in the similarity of K_π to K_σ and, for $\text{BaCuSi}_4\text{O}_{10}$, in comparison with the parameters observed for other oxygen-donor ligands towards Cu^{II} (see footnote † on p. 303).^{*} It thus seems likely that, in keeping with other planar complexes, the d_{z^2} orbital in these two complexes is significantly lowered in energy by configuration interaction with the metal $4s$ orbital. Indeed, in gillespite, it is probably only because of this interaction that the ground state is ${}^5A_{1g}$ rather than 5E_g . It will be interesting to see how angular-overlap parameters derived from other iron silicate minerals compare with those obtained in the present study.

High-pressure Form of Gillespite.—Above 26 kbar the structure of gillespite changes, the Fe-O bond lengths shortening slightly to 1.98 Å, and the co-ordination geometry alters to a highly flattened tetrahedron (O-Fe-O $\approx 167^\circ$).² The electronic spectrum of gillespite(II)

^{*} For instance, $K_\sigma = 8.79 \times 10^5\text{ cm}^{-1}$, $K_\pi(a) = 8.52 \times 10^5\text{ cm}^{-1}$, and $K_\pi(e) = 6.53 \times 10^5\text{ cm}^{-1}$ for the pentane-2,4-dionate anion towards Cu^{II} (M. A. Hitchman, *Inorg. Chem.*, 1974, **13**, 2222).

consists of peaks centred at *ca.* 17 200 and 7 150 cm^{-1} , *i.e.* the higher-energy peak undergoes a red shift of *ca.* 3 000 cm^{-1} , while the lower-energy peak shifts to lower energy by 1 100 cm^{-1} ; the transition to the 5E level is still unobserved above 6 000 cm^{-1} .⁶ The a.o.m. is ideally suited to calculate the d -orbital energy changes which should accompany the structural change. The shortening of the Fe-O bond produces a slight shift to higher energy of each of the d orbitals [S_σ 0.115 6, S_π 0.071 5 at 1.98 Å (footnote * on p. 303)]. The changes in the d -orbital energies as a function of the angle θ as the

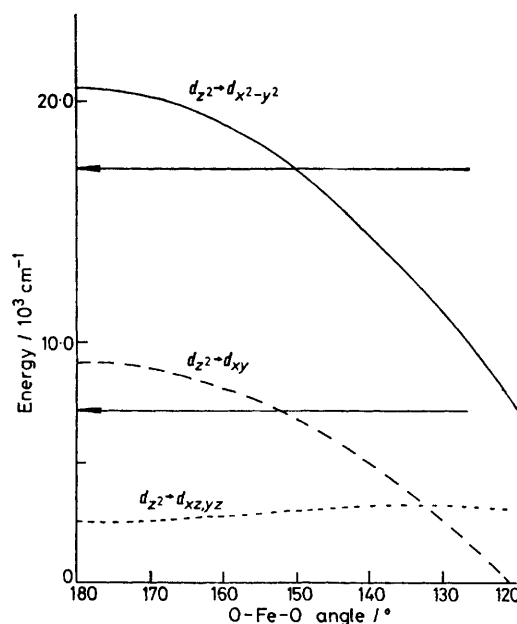


FIGURE 4 Variation of the ' $d-d$ ' transition energies as a function of the O-Fe-O angle on distortion of a planar iron(II) complex towards a tetrahedral geometry. The energies of the observed transition energies of gillespite(II) are indicated by arrows

complex distorts from a planar through to a tetrahedral geometry are readily calculated using equation (3),[†] and the concomitant shifts predicted in the $d-d$ energies are shown in Figure 4. The calculations were performed using the first set of angular-overlap parameters estimated for gillespite (those neglecting any $3d-4s$ mixing). A quite similar pattern is obtained using the second set of parameters if it is assumed that the energy depression due to the $3d-4s$ mixing decreases linearly with the distortion angle (*i.e.* the d_{z^2} orbital is lowered by 5 000 cm^{-1} at $\theta = 180^\circ$, with no lowering for a regular tetrahedron, where $\theta = 109.5^\circ$). An excellent fit to the observed spectrum of gillespite(II) is obtained, but at an angle O-Fe-O $\approx 150^\circ$ rather than the value of *ca.* 167° measured in the X-ray structure determination.² For small changes in θ the variation of the transition energies as a function of the distortion should be similar whatever

[†] Note that identical equations apply for a complex of C_{4v} symmetry and one in which a planar complex distorts towards a tetrahedral geometry. This results from the concept of holohedrized symmetry embodied in the a.o.m. (see ref. 9).

bonding model is used to parametrize the d -orbital energies since the dominant factor is the decrease in energy of $d_{x^2-y^2}$, which follows a $(1 - \cos\theta)^2$ dependence. In the crystal-structure determination of gillespite(II) the c axis co-ordinates of the oxygen atoms could not be determined directly (c is parallel to the z molecular axis).² The 'best' oxygen positions were therefore obtained by applying the constraints that the bond distance Si-O = 1.60 Å and that the non-bonding O-O distances exceed 2.45 Å. The final standard deviation in θ was $\pm 5^\circ$. It therefore seems plausible that the distortion on going from gillespite(I) to gillespite(II) is in fact considerably greater than that deduced from the X-ray structure determination.

Conclusions.—In agreement with previous studies of the electronic spectrum of gillespite, single-crystal magnetic-susceptibility measurements suggest that this mineral has a $^5A_{1g}$ ground state. Good agreement is obtained between the calculated and observed magnetic parameters of the compound over range 4.2–300 K using excited-state energies compatible with the measured electronic spectrum, although with a value of the orbital-reduction factor k considerably lower than expected. An analysis of the d -orbital energies in gillespite and its copper(II) isomorph using the angular-overlap model suggests the presence of a strong π -bonding interaction. More reasonable metal-ligand bonding parameters are obtained, however, if the $a_{1g}(3d_{z^2})$ orbital is lowered in energy by configuration interaction with the $a_{1g}(4s)$ orbital. It is shown that the electronic spectrum of the high-pressure form of gillespite is consistent with a distortion of the ligand oxygen atoms from a planar to a highly flattened tetrahedral geometry, but it is proposed that this distortion is likely to be considerably greater than that indicated in a previous X-ray crystal-structure determination.

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