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Authors
Wickman, H. Hollis
Klein, Melvin P.
Shirley, D.A.

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| Page | Line | Add: Spectra taken at 300\(^o\) K and 77\(^o\) K are shown in Fig. 3, and the more detailed spectra taken at 4.2\(^o\) K and 1.0\(^o\) K are shown in Fig. 4. |
PARAMAGNETIC RESONANCE OF Fe$^{3+}$ IN POLYCRYSTALLINE FERRICHROME A

H. Hollis Wickman, Melvin P. Klein and D. A. Shirley

September 1964
PARAMAGNETIC RESONANCE OF Fe$^{3+}$ IN POLYCRYSTALLINE FERRICHROME A

H. Hollis Wickman, Melvin P. Klein and D. A. Shirley

Department of Chemistry, Laboratory for Chemical Biodynamics and Lawrence Radiation Laboratory
University of California
Berkeley, California

September 1964

ABSTRACT

Polycrystalline samples of iron-containing Ferrichrome A, a cyclic hexapeptide obtained from the fungus Ustilago sphaerogena, have been investigated by paramagnetic resonance. Spectra were obtained at several temperatures between 300°K and 1°K; a prominent line of 400 Oe. width located at \( g = 4.3 \) was observed at all temperatures, while at 1°K additional resonances at \( g \) values of 9.6, 1.3 and 1.0 were observed. The spectra are interpreted by assuming a spin Hamiltonian containing crystal field terms large compared with the Zeeman splittings; the crystal field situation is intermediate between the case of axial symmetry, with \( H = D[S_x^2 - 1/3 \, S(S + 1)] + g\beta \, S \cdot H \) and a model proposed by Castner, Newell, Holton and Slichter to explain certain iron resonances occurring at \( g = 4.3 \), with \( H = E (S_x^2 - S_y^2) + g\beta \, S \cdot H \). We have computed \( g \) values, energy eigenvalues, and eigenfunctions to be expected for the region between these two extremes, and the results should be useful in interpreting similar spectra due to iron situated in strong crystal fields of low symmetry.
I. INTRODUCTION

The Ferrichrome A molecule is obtained from the smut fungus Ustilago sphaerogena, and although it is related in structure to substances that are growth factors in several microorganisms, its precise biological function is not known. Recently, Zalkin, Forrester and Templeton have determined the complete molecular structure, shown in Fig. 1, by x-ray diffraction with results in complete accord with those deduced from biochemical analysis. The coordination about the iron is roughly octahedral, resulting from the three hydroxamic acid residues, and is expected to have low overall crystal-field symmetry. The x-ray analysis confirms this, with the absolute configuration about the iron site shown in Fig. 2.

In Mössbauer resonance experiments on Ferrichrome A magnetic hyperfine structure was found in the Fe$^{3+}$ ion at temperatures as high as $77^\circ$ K, although the samples are certainly paramagnetic at least down to $1^\circ$ K. The paramagnetic resonance experiments reported herein, in Section II, were undertaken to provide us with a set of reasonably accurate eigenfunctions for the Fe$^{3+}$ in Ferrichrome A; these were required to make a detailed analysis of the relaxation phenomena encountered in the Mössbauer resonance studies.

While analyzing these experiments we have become aware of several symmetry properties of the spin Hamiltonian usually invoked to account for the strong resonances observed with a $g$ factor of 4.3 which are attributed to $^{6S_5/2}$ ions such as Fe$^{3+}$. Although these properties are really quite simple and are known to many, they have not always been completely exploited in interpretations of the paramagnetic resonance of such ions. Thus we have deemed it worthwhile to discuss, in Section III, the analysis of our spectra in somewhat greater detail than would otherwise be necessary. Finally in the Appendix, the eigenfunctions and eigenvalues of the spin Hamiltonian we propose are tabulated.
II. EXPERIMENTAL

A conventional superhetrodyne spectrometer operating at 9 kMc was used for all of the work reported here. All of the experiments were done with polycrystalline samples kindly provided by Prof. J. B. Neilands of the Biochemistry Department in Berkeley. The samples were isotopically enriched to $^{57}$Fe for Mössbauer studies. It will become clear in the next section that measurements on a single crystal would be highly informative; unfortunately, however, we have not yet been able to isolate a high quality crystal of size adequate for our spectrometer. We are continuing in these attempts.

At room temperature a strong resonance, of 400 Oe. linewidth, was observed at 1550 Oe. It has become customary to report paramagnetic resonance lines in terms of "g factors" which are in fact fictitious $g$ factors, $g'$, defined by assuming that the resonance in question arises from a doublet. A fictitious spin, $S'$, of 1/2 is associated with the doublet by equating its two-fold degeneracy to $2S' + 1$. The equation $g'S' = g_J$ relates $g'$ to the Landé $g$ factor $g_J$. For Fe$^3_\text{+}$ ($3d^5; \text{6S}_{5/2}$), $J$ is of course 5/2, and $g_J$ may be taken as 2.00, as it arises predominantly from electron spin. Following the usual convention we now drop the prime from the fictitious $g$ factor, and report this resonance as occurring at a $g$ of 4.3. This type of resonance is not unique to Ferrichrome A, but has been observed for Fe$^{3+}$ in several environments. The linewidth observed was greater by nearly a factor of ten than those previously reported and was not explicable by the usual interpretations.

Because the magnetic hyperfine structure in the Mössbauer spectra progressively became better resolved as the temperature was lowered, we were inclined initially to attribute the large linewidth of the paramagnetic resonance to a short electronic relaxation time. To minimize relaxation broadening we repeated the paramagnetic resonance experiments at temperatures down
to the helium range, without finding any qualitative changes, but at lower temperatures new resonant areas grow in. At 1.00 K there are particularly conspicuous resonances near \( g \) values of 1.0, 1.3 and 9.6. In some samples a small resonance was observed at \( g = 2.00 \) and was attributed to impurities.

It should be noted that the extreme linewidths encountered in these polycrystalline samples permit \( g \) value assignments of only moderate accuracy.

### III. DISCUSSION

Castner, Newell, Holton, and Slichter have given a clear discussion of the origins of an Fe\(^{3+}\) resonance at \( g = 4.3 \). In the interpretation of a spin resonance experiment on iron in glass they gave lucid arguments showing that a Hamiltonian of the form

\[
\mathcal{H} = E(S_x^2 - S_y^2) + g\beta \mathbf{H} \cdot \mathbf{S},
\]

(1)

with \( E \gg g\beta H \), will split a state with effective spin \( S = 5/2 \) into three doublets, of which the one of intermediate energy has an isotropic \( g \) value of 4.286. The reader is referred to their paper for the detailed development of this Hamiltonian, as well as for the basis of the present discussion.

Castner et al. noted that addition of a crystal field operator of the form \( D(S_z^2 - 1/3 S(S + 1)) \) to the above Hamiltonian has the effect, for \( D \ll E \), of broadening the line. Because the most outstanding unexplained feature of the Ferrichrome A spectrum was the broadness of the main line, and because the hyperfine structure of the Mössbauer spectra arose presumably from all the electronic levels of Fe\(^{3+}\), it seemed worthwhile to consider a Hamiltonian of the more general form.
\[ H = D(S_z^2 - \frac{1}{3} S(S + 1)) + E(S_x^2 - S_y^2) + g\beta H \cdot S = H_0 + g\beta H \cdot S \] \hspace{1cm} (2)

We shall assume for this discussion that the crystal field terms are large compared with the Zeeman terms. While consideration of operators of fourth order in the spin components, in addition to the second-order operators considered here, would constitute a more complete approach to the problem, our polycrystalline-sample data hardly warrant this additional sophistication, and certainly do not require it. At the same time \( H_0 \) is the most general crystal field Hamiltonian of second powers of spin operators. We shall find it convenient to define the parameter \( \lambda = E/D \) and to write \( H_0 \) in units of \( D \),

\[ H_0 = S_z^2 - \frac{1}{3} S(S + 1) + \lambda (S_x^2 - S_y^2) \] \hspace{1cm} (3)

On diagonalizing \( H_0 \) in the \( J = \frac{5}{2} \) manifold of the Fe\(^{3+} 3d^5 \s_5/2 \) level, we find three Kramers' doublets \( \psi^\pm \), given in \( |J_z\rangle \) representation by

\[ \psi^\pm_i = a_i |\pm \frac{5}{2}\rangle + b_i |\pm \frac{1}{2}\rangle + c_i |\pm \frac{3}{2}\rangle, \] \hspace{1cm} with \( i = 1, 2, 3 \). \hspace{1cm} (4)

The \( a_i \), \( b_i \), and \( c_i \) are functions of the single parameter \( \lambda \). The range of physically distinct values for \( \lambda \) is restricted to \( \lambda \leq \frac{1}{3} \). In addition, only positive values of \( \lambda \) need be considered. These symmetries are most easily displayed by writing \( H_0 \) in the form

\[ H_0 = A S_x^2 + B S_y^2 + C S_z^2 \] \hspace{1cm} (5)

with \( A + B + C = 0 \). A coordinate system may be chosen such that \( |C| \geq |B|, |A| \), and it is always possible to choose \( B > A \). In this system \( H_0 \) assumes
the conventional form after the substitutions \( C = 2D/3 \), \( B = E - D/3 \), \( A = -E-D/3 \). Now we see \( \lambda = E/D = (B-A)/3C \), or \( |\lambda|<1/3 \), since \( |B-A|<|C| \). With our choice of \( A \), \( B \), and \( C \), we find that \( E \) is always positive. Thus the sign of \( \lambda \) determines the sign of \( D \). By diagonalizing \( H_0 \) for positive \( \lambda \) in the range \( 0 \leq \lambda \leq 1/3 \) we obtain the complete range of physically distinct eigenvalues and eigenfunctions for \( D > 0 \). For \( D \leq 0 \) we need only invert the energy levels. A positive \( D \) means, of course, that in the limit \( \lambda = 0 \) the state \( |S_z = \pm 1/2\rangle \) lies lowest in energy.

We have plotted in Fig. 5 the variation with \( \lambda \) of the effective \( g \) factors for the three crystal-field Kramers' doublets considered separately as having effective spins of \( 1/2 \). In the Appendix eigenfunctions and energy eigenvalues are given in tabular form. We note that Castner et al. used the Hamiltonian \( \mathcal{H} = E(S_x^2 - S_y^2) \), which is identical aside from a scale factor and a rotation of axes to \( H_0 \) with \( \lambda = 1/3 \). This is easily checked by substituting \( 1/3 \) for \( \lambda \) in Eq. (3), and replacing \( S(S + 1) \) by \( S_x^2 + S_y^2 + S_z^2 \). Thus while the description of a Hamiltonian as having only a \( D \) term is physically meaningful, implying axial symmetry, it is never necessary to invoke a crystal-field Hamiltonian with only a large \( E \) term and \( D = 0 \). This is one example of a physical problem in which one may or may not choose to order the principal axes of the system according to the magnitude of the influence of the Hamiltonian in each direction; if one does so choose, \( E \) need never be larger in magnitude than \( D \). An analogous case occurs in nuclear quadrupole interaction, for which an asymmetry parameter \( \eta \) is introduced to describe deviations from axial symmetry, and \( \eta \) need never exceed unity.

From Fig. 5 we find that the variation of the upper-level \( g \) values is small. In the middle level the \( g \) values vary from highly anisotropic to isotropic as \( \lambda \) increases from 0 to \( 1/3 \). For the lower level the \( g \) values
vary considerably and assume the same values at \( \lambda = 1/3 \) as those of the upper level, except for a relabeling of the axes. (There is complete symmetry between the \( g \) values of the different levels for the ranges \( 0 \leq \lambda \leq 1/3 \) and \( 1/3 \leq \lambda \leq 1 \), within trivial relabeling and a scale factor in \( \lambda \). In fact by combining these two ranges we exhaust all the distinct physical possibilities for the system including both signs for \( D \). This may easily be shown analytically by reference to the Hamiltonian, Eq. (3).) If higher-order crystal-field operators may be neglected, the calculation summarized by Fig. 5 should suffice to account for the dominant features of the resonance data. Let us first consider the linewidth of the main "isotropic" line at \( g = 4.3 \). The absorption actually occurs over the range \( g = 4.3 + 0.67 \), taking the crossing point, maximum, and minimum in the derivative curve. This is consistent with a \( |\lambda| \) of 0.23, for which three closely-spaced lines are expected. In a polycrystalline sample spectrum these would appear as a broad resonance at approximately the average of their \( g \) values.

This value of \( \lambda \) requires the appearance of lines originating from the lower level; the principal values at \( \lambda = 0.23 \) for the effective \( g \) tensor of this level are 9.3, 1.7, and 1.0. These lines are expected even in polycrystalline samples, because their intensities are derived from the large \( g_y \) of 9.3 in this level. Indeed the lowest temperature spectra show features of this type, namely the "humps" at 9.6, 1.3, and 1.0. The growth of these absorptions with decreasing temperatures establishes \( \lambda \) (and thus \( D \)) as positive. The lack of accurate agreement is probably due in part to the inherent difficulty of assigning \( g \) values based on a broad resonant area extending over a region of 7000 gauss. Again, neglect of the Zeeman energy, with consequent admixing of higher doublets, is less valid in the high-field region. The observed linewidth of the main resonance is compatible with a range of about 0.10 in \( \lambda \), and the fit to experiment of the principal values of the
lower-level $g$ tensor may be improved somewhat by varying $\lambda$. For example, a $\lambda$ of 0.25 gives $g$ values of 9.45, 1.32, and 0.86. Even without an exact fit and in spite of the various approximations discussed above, our data require $\lambda$ to be in the range $\lambda = 0.25 \pm 0.04$.

While it was not possible, in view of the complexity of the spectra, to get an accurate experimental determination of the energy spacing between the two lowest doublets, the relative intensities of the different absorption regions at different temperatures yield a very rough estimate of $5^0 K$ for this parameter, $(E_2 - E_1)/k$. This estimate is consistent with the Mössbauer experiments.

A very much more detailed study of the magnetic properties of Ferrichrome A would be possible, and obviously highly desirable, if a single crystal were available. In particular it would be interesting to test experimentally the assumptions made in the present analysis. This analysis, and especially the eigenfunctions and eigenvalues given in the Appendix, may prove useful in analyzing magnetic resonance spectra of Fe$^{3+}$ in similar environments.

We are indebted to Prof. J. B. Neilands both for eliciting our interest in Ferrichrome A and for providing the samples used in this work. Dr. R. A. J. Warren kindly incorporated the Fe$^{57}$ into the samples. We should also like to express our gratitude to Drs. T. Castner and K. W. H. Stevens for pointing out an error in a previous calculation and thus making possible the present interpretation.
APPENDIX

We have set out in Table I the eigenfunctions and eigenvalues of the Hamiltonian

$$\mathcal{H}_0 = \frac{S_z^2}{2} - (1/3) S(S + 1) + \lambda (S_x^2 - S_y^2),$$

for the case $S = 5/2$. This is equivalent to the customary form

$$\mathcal{H}_0 = D(S_z^2 - (1/3) S(S + 1)) + E(S_x^2 - S_y^2),$$

with $\lambda = E/D$, and with energy units of $D$. We choose the axes in such a way that $E$ is always positive. Thus we need only solve for $\lambda$ in the range $0 \leq \lambda \leq 1/3$, corresponding to positive $D$. The solutions for negative $D$ are obtained from these by simply changing the signs of the energy eigenvalues.

The principle values of the effective $g$-factor tensor are given by the equations

$$g_{x,1} = g_J(3b_1^2 + 2\sqrt{5} a_1 c_1 + 4\sqrt{2} b_1 c_1),$$

$$g_{y,1} = (-1)^{1+1}g_J(3b_1^2 + 2\sqrt{5} a_1 c_1 - 4\sqrt{2} b_1 c_1),$$

$$g_{z,1} = (-1)^{1+1}2g_J(5a_1^2/2 + b_1^2/2 - 3c_1^2/2).$$

Here the subscripts $x, y, z$, denote coordinate axes. The subscripts $i = 1, 2, 3$ label the three doublets. We have taken $g_J = g_S = g_{5/2} = 2.00$ for Fig. 5.
Table I. Eigenfunctions and eigenvalues of energy for the Hamiltonian $\frac{1}{2} S^2 - \frac{1}{3} S(S + 1) + \lambda (S_x^2 - S_y^2)$. Eigenfunctions are written in the notation $\psi_i = a_i | S_z = \pm \frac{3}{2} \rangle + b_i | S_z = \pm \frac{1}{2} \rangle + c_i | S_z = \pm \frac{1}{2} \rangle$.

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REFERENCES

* Work performed under the auspices of the United States Atomic Energy Commission.

† Present address: Bell Telephone Laboratories, Inc., Murray Hill, N. J.

3. A. Zalkin, J. D. Forrester, and David H. Templeton, UCRL-11461.
4. H. Hollis Wickman, Melvin P. Klein, and D. A. Shirley, to be published.
FIGURE CAPTIONS.

Figure 1. The Ferrichrome A molecule. The dashed lines indicate hydrogen bonds which are operative in the solid.

Figure 2. The absolute configuration of the ligand atoms surrounding the Fe$^{3+}$ ion in Ferrichrome A, after Zalkin, Forrester, and Templeton.

Figure 3. The X-band paramagnetic resonance spectrum of Ferrichrome A observed at 300° K and at 77° K. The curve is a plot of dX"/dH.

Figure 4. The X-band paramagnetic resonance spectrum of Ferrichrome A observed at 4.2° K and at 1.0° K. The curve is a plot of dX"/dH.

Figure 5. The effective g values for the spin-Hamiltonian

$$\mathcal{H} = D S_z^2 - \frac{1}{3} S(S+1) + E(S_x^2 - S_y^2)$$

operating within a \( J = \frac{5}{2} \) manifold, (with \( g_J = 2.00 \), plotted against \( \lambda = E/D \). Except for the order of the energy levels, the range \( 1/3 \leq \lambda \leq 1 \) is redundant. The symmetry around \( \lambda = 1/3 \) is easily displayed by changing the sign of \( D \) (thus inverting the order of the levels), making the transformation \( y \rightarrow x, \ z \rightarrow y, \ x \rightarrow z \), and substituting \( \lambda' = 1 - 2\lambda \) for \( \lambda \).
Fig. 1
Left-handed Coordination
Propeller About Fe In Ferrichrome-A
Fig. 3
Fig. 4
Fig. 5
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