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# Spin-3/2 Iron Ferromagnet: Its Mössbauer and Magnetic Properties

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A spin-$\frac{3}{2}$ ferromagnetic iron compound is reported. The ferromagnet is bis-($N$, $N$-diethyldithiocarbamato) iron$^{\text{III}}$ chloride, and has a Curie temperature of 2.5°K. Extensive susceptibility, ESR, and Mössbauer data are presented which establish conclusively that the ground electronic state of iron in this system is a spin quartet, $S=\frac{3}{2}$. This behavior is uncommon for iron, and the present system is apparently the initial instance of a spin-$\frac{3}{2}$ iron ferromagnet. The iron in this complex is pentacoordinate, with site symmetry $C_{2V}$, as shown by Hoskins, Martin, and White. A consideration of the ligand field problem associated with this symmetry suggests the origin of the quartet ground term. The effects of relaxation phenomena in the ferromagnetic state have been observed in some of the Mössbauer spectra.

The magnetic properties of trivalent iron magnetic systems are well known and have been extensively investigated for many years.[1] The five spins of the $Fe^{3+}$ $3d^5$ configuration may be coupled to yield a maximum and minimum total spin of $\frac{5}{2}$ and $\frac{1}{2}$, respectively. Examples of these two situations are common and are termed, respectively, high- or low-spin iron complexes. In addition, however, a total spin of $\frac{3}{2}$ may also occur and in this paper we report this behavior in a new iron ferromagnet, bis-($N$, $N$-diethyldithiocarbamato) iron$^{\text{III}}$ chloride ($T_c=2.5$°K). While great effort has been expended on the study of magnetic iron systems, the present work apparently represents the first detailed magnetic investigation of an iron ferromagnet with essentially spin only magnetic character, and $S=\frac{3}{2}$. This state is forbidden, for example, in cubic symmetry, and only limited discussion of the general conditions under which it may occur has been given.[2] We briefly mention below an approximate level system appropriate to the present case, but mainly offer detailed data concerning the magnetic properties of the system.

The crystal structure of the metallorganic compound, abbreviated as $Fe(diEt\text{-}DTC)_2Cl$, was recently studied by Hoskins, Martin, and White.[3] These authors have also concluded, on the basis of susceptibility measurements from 130 to 300°K, that $S=\frac{3}{2}$ for the iron in tion shows that the $Fe(diEt\text{-}DTC)_2Cl$ crystal consists of discrete molecules with 4 molecules per unit cell.[3] The trivalent iron is covalently bound in the approximate center of a pyramid with a rectangular base of 4 sulfur atoms and apex of one chlorine atom. The iron is 0.63 Å above the plane of the sulfur atoms. The local symmetry is therefore $C_{2V}$, in contrast with the common cases of higher symmetries such as octahedral, tetrahedral, etc. A single-crystal x-ray diffraction study of the material used in these experiments showed a monoclinic unit cell with $a=16.41°$, $b=9.40°$, $c=12.85°$, and $\beta=120.2°$. These data are in excellent agreement with the results of Hoskins, Martin, and White.[3]

It is useful at this point to comment briefly on the characteristics of the present system which influence strongly the magnetic properties of the iron complex. Griffith, in an analysis of the ESR of ferric porphyrin chloride, suggested that under some circumstances a quartet term may be stabilized in strong ligand fields of $D_4$ symmetry, although the quartet term is forbidden in octahedral symmetry.[2] With $C_{2V}$ symmetry, the following arguments may be used to make a zero-order strong ligand field assignment; we neglect for the moment electrostatic and spin-orbit interactions and covalency. The strong field octahedral orbitals, $e_g$:$d_{z^2}$, $d_{x^2-y^2}$, and $t_{2g}$:$d_{xy}$, $d_{xz}$, $d_{yz}$, are natural bases for the $C_{2V}$ representations. The Fe-Cl direction is the $z$ direction and the $x$ axis is parallel to the long $S$-$S$ direction and contains the iron atom. The $e_g$ and $t_{2g}$ orbitals are split under $C_{2V}$ and become $a_1$:$d_{x^2-y^2}$, $a'_1$:$d_{z^2}$, $a_2$:$d_{xy}$, $b_1$:$d_{xz}$ and $b_2$:$d_{yz}$. Five paramenters are, in general, required to specify completely the $C_{2V}$ field for $d$ electrons and the relative order of the states is uncertain, with one important exception which is of a qualitative nature and should be reasonably independent of the strong $C_{2V}$ field. The usual point-charge considerations show that the $a_2$:$d_{xy}$ orbital is greatly destabilized by the ligand field and is expected to lie far above the four remaining levels by an energy large compared to interelectronic and spin-orbit energies.

The above discussion leads to a grouping of four ligand field levels which yield the ground configuration. Similar electrostatic arguments suggest the ground configuration be given as $a_1^2 b_2^1 b_1^1 a'^1_1$, whose "Hund" ground term is a spin quartet. We emphasize that, so far, only a heuristic scheme has been given, and it is well known that inclusion of electrostatic and spin-orbit interactions is necessary for a more complete description. This will lead to the situation where the ground term does not derive from a single configuration, and may be a complex mixture. This has been shown for example by Harris discussion of low spin ferric complexes.[4] Another description of the present com-

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[1] J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience Publishers, Inc., New York, 1963).

[2] J. S. Griffith, *The Theory of the Transition Metal Ions* (Cambridge University Press, New York, 1961); J. S. Griffith, Discussions Faraday Soc. **26**, 81 (1958).

[3] B. F. Hoskins, R. L. Martin, and A. H. White, Nature **211**, 627 (1966).

[4] G. Harris, Theoret. Chim. Acta **5**, 379 (1966).

pound would utilize the molecular orbital approach, and from this analysis should come a clearer picture of the relative spacing of the four ground levels mentioned above in the ligand field framework. However, such analyses depend critically on the experimental data for the iron complex and we now turn to its magnetic properties.

The bulk dc susceptibility of Fe(diEt-DTC)$_2$Cl was measured as a function of temperature from 1.4 to 300°K; the results (truncated for clarity to show the susceptibility for $1.45 \leq T \leq 200$°K) are shown in Fig. 1. These data indicate a well-behaved paramagnet with susceptibility described by a Curie-Weiss law, and a paramagnetic Curie temperature of 3.6°K. In the paramagnetic region, the effective ionic moment of the iron complex is 4.03 $\mu_B$. This is slightly higher than the theoretical value of $3.87\mu_B$ for $S=\frac{3}{2}$ and $g=2$. A moment larger than the spin-only value may indicate a small orbital contribution to the total moment. More detailed susceptibility data were also obtained at several temperatures from 1.46 to 7.0°K and varying magnetic fields. These results are shown in Fig. 2. Large deviations from Brillouin function behavior were found; particularly striking is the ease of relative saturation of the iron moment.

To determine the transition temperature more accurately, a polycrystalline sample was placed in the tank coil of an oscillator normally used for detecting superconductivity, and the relative ac susceptibility (detected as a frequency shift in the resonant circuit) in zero field was determined as a function of temperature from 0.3 to 17°K. A typical ac measurement is shown in Fig. 3, and from these data the transition temperature 2.5°K is assigned.

Electron-spin-resonance measurements at 24 GHz were employed to investigate a relatively large (1.5 mm$^3$) single crystal that was also used in the x-ray study. For $T \leqslant 20$°K, a strong change in susceptibility of the sample was detected as a function of the applied field (to 14 kOe). The signal increased in intensity rapidly with decreasing temperature until at $T \lesssim T_c$ and depending on the sample orientation, a strong ferromagnetic-type resonance was observed. Unlike the case of an homologous paramagnetic iron system (Fe(diisopropyl-DTC)$_2$Cl) where clear ESR results ascribable to a resonant doublet in an $S=\frac{3}{2}$ manifold were observed,[5] no strong resonances at temperatures greater than 77°K were found.[6]

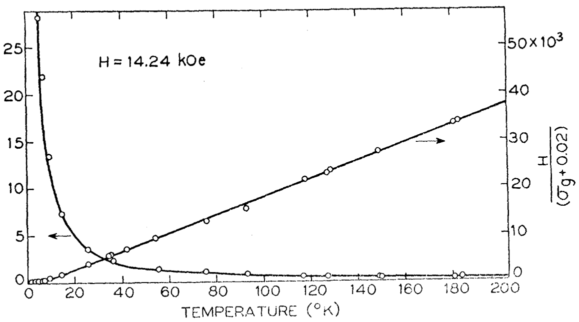

FIG. 1. Magnetization as a function of temperature for Fe(diEt-DTC)$_2$Cl. The ordinate to the right applies to the straight line representing the Curie law dependence in the paramagnetic region. The small diamagnetic correction is shown in the figure.

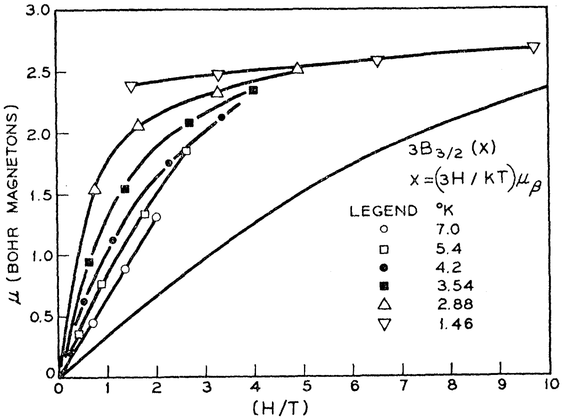

FIG. 2. Magnetization curves at several fields and temperatures. The solid line without markers is a Brillouin function for a spin of $\frac{3}{2}$. The units for $H/T$ are kOe/°K.

Mössbauer studies with polycrystalline absorbers containing naturally abundant Fe$^{-57}$ were performed with absorber temperatures from 1.6 to 300°K. A slightly temperature-dependent quadrupole doublet was observed from 77 to 300°K. The low-temperature data, $T \leq 4.2$°K, will be given here (Fig. 4). The splitting at 4.2°K is 0.268 cm/sec. Below 3.0°K and through the transition region (2.5°K), the Mössbauer lines are quite broad and at some temperatures ill defined. It is not possible to distinguish completly between (1) broadening due to incipient magnetism in a direction noncollinear with an electric field gradient (EFG) axis, and (2) broadening due to relaxation effects. However, it is probable that relaxation is important in both the paramagnetic and ferromagnetic regions near the transition point in this system.[7,8] Even well into the ferro-

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[5] H. H. Wickman, F. R. Merritt, and A. M. Trozzolo (to be published). Single crystal studies of Fe (diisopropyl-DTC)$_2$Cl show a prominent anisotropic resonance with effective $g$ values $g_z=2.0\pm0.05$, $3.8<g_x$, $g_y<4.2$, corresponding to a doublet $\sim |S=\frac{3}{2}, M_S \pm\frac{1}{2}\rangle$, which has theoretical effective $g$ values with $g_{\parallel}=2.0$ and $g_{\perp}=4.0$ for $g_L=2.00$.

[6] We have observed the ESR of large polycrystalline samples of a Fe(diEt-DTC)$_2$Cl at $X$ band (10 GHz) at 300 and 77°K. The spectrum consists of an envelope corresponding to $g=2$ and $g=4$.

[7] Relaxation effects were observed in an early study of Fe(dimet-DTC)$_2$Cl and Fe(diisopropyl-DTC)$_2$Cl. [H. H. Wickman and A. M. Trozzolo, Phys. Rev. Letters **15**, 156 (1965). Erratum **16**, 162 (1966)]. Relaxation times in these paramagnetic homologues are longer at a given temperature than those in Fe(diEt-DTO)$_2$Cl. This argues for stronger dipolar or exchange interactions in the latter system; and is consistent with the magnetic ordering of the Fe(diEt-DTC)$_2$Cl.

[8] For a recent discussion of ferromagnetic relaxation effects in Mössbauer spectra see I. Nowik and H. H. Wickman, Phys. Rev. Letters **17**, 949 (1966), and references therein.

magnetic region (e.g., 2.2°K data), the Mössbauer lines are broadened considerably. It is difficult to compute theoretical Mössbauer relaxation spectra for the present experimental circumstances.[7,8] However, one interesting qualitative conclusion that can be drawn from the data of Fig. 4 is that relaxation times do not change drastically on passing from the paramagnetic to the ferromagnetic region.

As the temperature is decreased, the relaxation times and/or populations change sufficiently to produce a well defined Mössbauer hfs. Analysis of the 1.6°K data shows several interesting features. First, the magnetic hyperfine field is 329±10 kOe. This is in remarkably good agreement with the field of 330 kOe expected for a $|M_S|=\frac{3}{2}$ state, using the empirical relation for *high* spin $Fe^{3+}$, $H_{\text{eff}}=220\langle S_z\rangle$.[9] This result indicates that the effects of covalency in the ground state are not sufficient to alter greatly the spin-only character of the ground level. Any orbital contribution to the total moment, possibly suggested by the susceptibility data, must be small. Second, the relative intensities of the six hyperfine lines (2.86:1.41:1.63:1.80: 1.52:2.77) are not in agreement with the common case (3:2:1:1:2:3) corresponding to a collinear hyperfine magnetic field and axially symmetric electric field gradient (EFG). This observation is in agreenent with the symmetry, $C_{2V}$, which implies an EFG with $\eta\neq 0$. *Note added in proof.* Additional Mössbauer experiments have shown that microcrystals of Fe(diEt–DTC)$_2$Cl, when pressed in an absorber holder, tend to orient themselves with the result that the magnetic hyperfine fields are geometrically nearly perpendicular to the gamma-ray direction. The intensities of Fig. 4 are therefore characteristic of a partially "polarized" absorber. With finely powdered material a random absorption pattern is found for which the best available fit for the conventional quadrapole parameters are: $(e^2qQ/4)=0.134$ cm/sec and $\eta=0.14$. The principle axis of the EFG tensor is perpendicular to the hyperfine magnetic field direction.

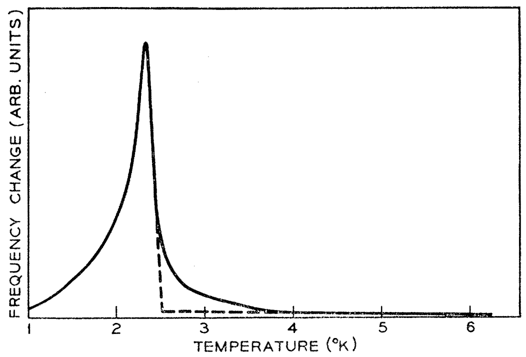

FIG. 3. Relative ac susceptibility in zero field as function of temperature. The transition temperature of 2.5°K is based on the intersection of the two asymptotes as shown in the figure.

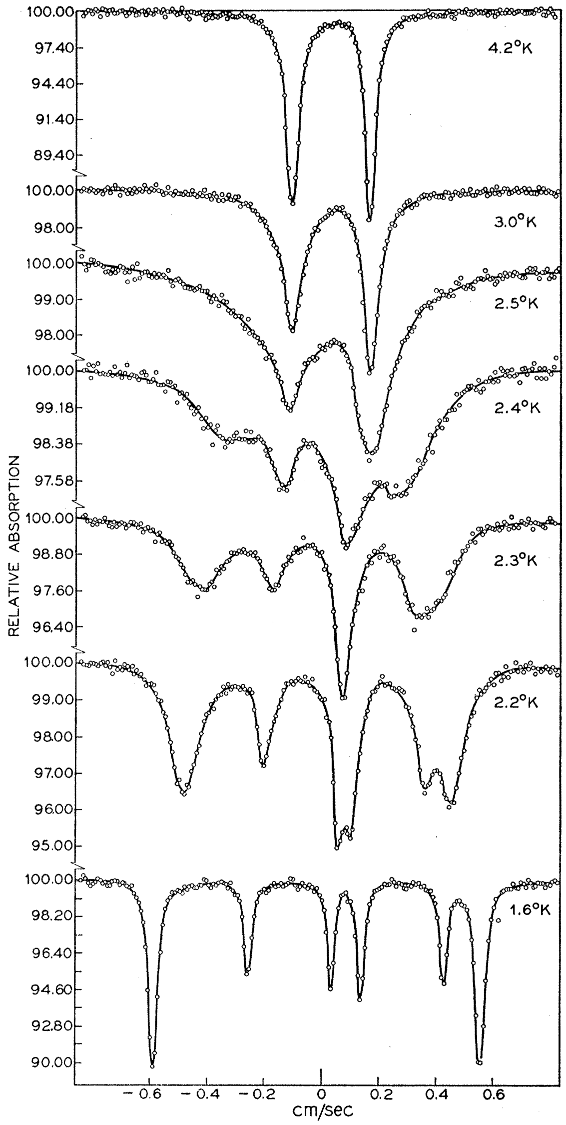

FIG. 4 Mössbauer absorption spectra Fe(diEt-DTC)$_2$Cl as a function of temperature, $1.6\leq T\leq 4.2$.

The low-ordering temperature and Van der Waals-type molecular arrangement in the crystal lattice make it likely that dipolar interactions and weak exchange interactions represent the main mechanisms for the magnetic ordering. Determination of the dominant interaction and the type of exchange involved requires knowledge of the finer mechanism of the ferromagnetic interaction and is currently under study. In conclusion, we note that in order to determine the effect of structure on the ferromagnetic properties of Fe(diEt-DTC)$_2$Cl, we are replacing the chloride by other halide groups

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[9] G. K. Wertheim, and J. P. Remeika, Phys. Letters **10**, 14 (1964).

and also varying the alkyl groups attached to the nitrogen of the dithiocarbamates. It is probable that with structural changes such as these, additional spin-$\frac{3}{2}$ ferromagnets will be found.

We would like to acknowledge several useful discussions with G. K. Wertheim during the course of this work. The able assistance of C. F. Wagner during the Mössbauer measurements is greatly appreciated.

# Errata

**Nuclear Magnetic Resonance in the Paramagnetic States of MnO, α-MnS, and α-MnSe,** E. D. JONES [Phys. Rev. **151**, 315 (1966)]. The hyperfine coupling constant for MnO at 4.2°K, given in Table I, should be $-83.51\pm0.01$.

**Magnetic Irreversible Solution of the Ginzburg-Landau Equations,** H. J. FINK AND A. G. PRESSON [Phys. Rev. **151**, 219 (1966)]. 1. The value of $\alpha$ defined by Eq. (12) is not of order unity, as stated on p. 221, second column, first line, but equal to $(\chi/\kappa)\beta$, where $\beta$ is of order unity and defined by Eq. (13) in Ref. 6. This changes the conclusions in lines 15 to 19 counted backward from the end of Sec. II. It makes the lowest energy of the giant-vortex state energetically more favorable than the mixed state for larger values of $\chi$. For example, for $\chi=100$ and $\kappa$ equal to $\infty$, 3, 1.5, 1.0, the respective values of $H_{0s}/H_{c2}$ are 1.0, 0.93, 0.89, 0.84. 2. The term on the ordinate of Fig. 11 should read

$$H_{c1}/\sqrt{2}\kappa H_c.$$

**Quantum Theory of Laser Radiation. I. Many-Atom Effects,** J. A. FLECK, JR. [Phys. Rev. **149**, 309 (1966)]. The following misprints should be corrected: In the second of Eqs. (3.6) $\omega_a$ should be changed to $\omega_b$. In Eq. (3.20) the first $\eta_b$ should be changed to $\eta_a$. In the calculation using Eq. (6.11) described in Sec. X a loss term $-\gamma_c\langle n\rangle$ was included on the right-hand side of the equation.

**Quantum Theory of Radiation. II. Statistical Aspects of Laser Light,** J. A. FLECK, JR. [Phys. Rev. **149**, 322 (1966)]. The following misprints should be corrected: The second $N_b$ which appears on the right-hand side of Eqs. (2.1a), (2.1b), and (2.2a) should be changed to $N_a$. The signs of the last two terms in Eq. (2.2a) should be reversed. The $\gamma$ appearing in Eqs. (5.4) and (5.5) should be changed to $\gamma_c$.

**Conduction Electron Spin Resonance,** M. LAMPE AND P. M. PLATZMAN [Phys. Rev. **150**, 340 (1966)]. The caption to Fig. 1 should read $X\equiv(\omega_s/\omega-1)\omega T$. In addition Eq. (16) and Eq. (24) should now read:

$$G(z,z',t')=\frac{1}{L}\sum_{n=-\infty}^{\infty}\cos\mu_n z\cos\mu_n z'\exp\left(-\frac{1}{3}\frac{\Lambda^2}{\tau}\mu_n{}^2t'\right) \quad (16)$$

$$a^2=\frac{3L^2}{2\Lambda^2}\frac{\tau}{T}\equiv\frac{L^2}{\delta_{\mathrm{mag}}{}^2} \quad (24)$$

**Nuclear Magnetic Resonance Local-Magnetic-Field Shift in Solid Xenon,** JOAN LURIE, JOSEPH L. FELDMAN, AND GEORGE HORTON [Phys. Rev. **150**, 180 (1966)]. The second line of Eq. (4) (p. 181) reads:

$$\times\sum_{\mathrm{n.n.}}\left\langle\sin^2\theta\left[1+\frac{Z^2(\mathbf{u}\cdot\mathbf{R}_0)^2}{2R_0{}^2}-\frac{Z}{2R_0}\frac{\mathbf{u}^2-(\mathbf{u}\cdot\mathbf{R}_0)^2}{R_0{}^2}\right]\right\rangle$$

but should read:

$$\times\sum_{\mathrm{n.n.}}\left\langle\sin^2\theta\left[1+\frac{Z^2(\mathbf{u}\cdot\mathbf{R}_0)^2}{2R_0{}^2}-\frac{Z}{2R_0}\left(u^2-\frac{(\mathbf{u}\cdot\mathbf{R}_0)^2}{R_0{}^2}\right)\right]\right\rangle.$$

The expression two lines below Eq. (6) (p. 182) reads

$$\left.\frac{\partial^2\phi}{\partial r^2}\right|_{R_0(T)}=f_3=\cdots$$

but should read:

$$\left.\frac{\partial^2\phi}{\partial r^2}\right|_{R_0(T)} \quad \text{and} \quad f_3=\cdots.$$