A Re-examination of Bis(tetramethylammonium) Tetrachloroferrate(II) by Mössbauer Spectroscopy

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A re-examination of $[NMe_4]_2[FeCl_4]$ by Mössbauer spectroscopy has revealed the presence of a phase transition at 239 K. The temperature dependence of the quadrupole splitting deviates markedly from theoretical prediction on the basis of a tetragonal distortion. Possible causes are discussed including in particular the effects of vibronic interactions.

In an earlier paper [1] we showed that the temperature dependence of the quadrupole splitting in the Mössbauer spectrum of a tetrahedrally co-ordinated iron(II) ion could be simply related to the tetragonal distortion of the tetrahedron. An example of this was found in $[NEt_4]_2[FeCl_4]$. Subsequently, Edwards *et al.*[2] carried out a major investigation of several compounds containing $[FeX_4]^{2-}$ anions, including in particular the complex $[NMe_4]_2[FeCl_4]$ for which they found substantial deviations from theoretical prediction. In this paper we report a re-investigation of this compound which has revealed the existence of a hitherto unreported phase transition and allows a more satisfactory analysis of the experimental data. In addition, the possible effects on the Mössbauer spectrum of vibronic interaction in a tetrahedral iron(II) ion are considered.

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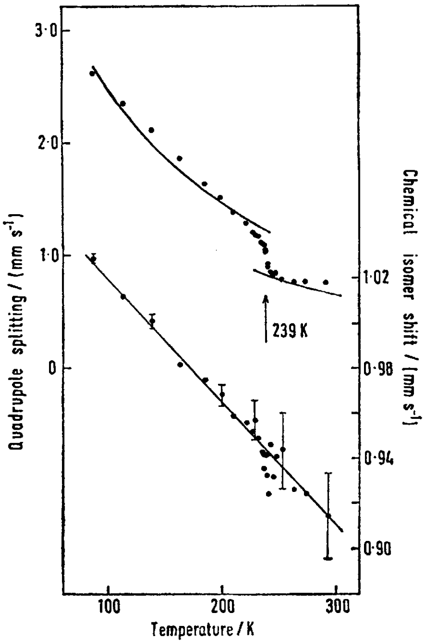
[1] T. C. Gibb and N. N. Greenwood, *J. Chem. Soc.*, 1965, 6985.

[2] P. R. Edwards, C. E. Johnson, and R. J. P. Williams, *J. Chem. Phys.*, 1967, **47**, 2074.

RESULTS AND DISCUSSION

A sample of $[NMe_4]_2[FeCl_4]$ was prepared by standard methods,[3] and the Mössbauer spectra were recorded in the temperature range 87—292 K with equipment described in detail in an earlier paper.[4] The quadrupole splitting and chemical isomer shift values are shown in the Figure. The percentage absorption obtained from a given absorber matrix decreases markedly with rising temperature (by a factor of 10 in the range studied), resulting in substantially larger standard deviations above 200 K. However, the data are self-consistent and show conclusively the presence of a discontinuity in the quadrupole splitting at 239 ± 1 K. This feature was overlooked by Edwards *et al.*[2] and contributed to their difficulties in interpreting the experimental data. There is however no discontinuity in the chemical isomer shift.



The temperature dependence of the quadrupole splitting and chemical isomer shift relative to iron metal in $[NMe_4]_2[FeCl_4]$. At temperatures below 239 K the solid line represents the theoretical prediction for a tetragonal distortion of 132 cm^{-1}, while above 239 K the distortion is 84 cm^{-1}

The most obvious interpretation of the discontinuity in the quadrupole splitting data is that a phase transition occurs at 239 K. The *X*-ray powder diffraction patterns at room temperature and at *ca.* 90 K were therefore obtained. These show substantial differences and confirm that a transition has taken place, but there are obvious difficulties in growing single crystals of both phases and we have not continued this line of investigation.

Magnetic susceptibility data between 120 and 320 K showed no anomaly around 239 K, implying that any change in the crystal field at the Fe^{2+} ion during the phase transition was quite small. Presumably the $[FeCl_4]^{2-}$ ion is not strongly affected by the change, although the lack of an orbital contribution from the ^5E ground state makes this an insensitive criterion.

The orbital degeneracy of the ^5E ground state of tetrahedrally co-ordinated Fe^{2+} can be removed by a tetragonal distortion of the tetrahedron. The resulting non-degenerate states are conventionally represented as $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ and cannot mix under the influence of either the tetragonal field or spin–orbit coupling, remaining 'pure' states with an energy separation of ξ. The temperature dependence of the quadrupole splitting is determined quite simply by thermal population of these two levels,[1,2] and may be represented by

$$\Delta(T) = \tfrac{2}{7}e^2Q\,\langle r^{-3}\rangle\,\frac{1 - e^{-\xi/kT}}{1 + e^{-\xi/kT}}$$
$$= \tfrac{2}{7}e^2Q\,\langle r^{-3}\rangle \tanh(\xi/2kT) \qquad (1)$$

where Q is the nuclear quadrupole moment, $\langle r^{-3}\rangle$ is a radial expectation value for the $3d$ electron, T is the temperature, e is the charge on the proton, and k is Boltzmann's constant.

Edwards *et al.* attempted to fit their data with this function. Although they derived parameters of $\Delta(T = 0) = 3{\cdot}25$ mm s^{-1} and $\xi = 125$ cm^{-1}, there were large deviations unaccounted for. This was partly due to the failure to observe the phase transition. We have analysed our data in two parts. Below 239 K, parameters of $\Delta(T = 0) = 3{\cdot}36$ mm s^{-1} and $\xi = 132$ cm^{-1} (190 K) produce the solid line shown in the Figure. Above 239 K, a reduction in ξ to 84 cm^{-1} (120 K) produces the other line. It is therefore possible to explain the sudden decrease in quadrupole splitting at 239 K as symptomatic of a reduction in the tetragonal distortion in the tetrahedron. However, this viewpoint is obviously too naive to be the whole explanation.

Both Edwards *et al.* and we have found the observed quadrupole splitting to be linearly dependent on the temperature in the region 90—220 K, whilst the nature of the $\tanh(\xi/2kT)$ function demands considerable curvature in the relationship. It is not possible to account for this behaviour by inclusion of a temperature-independent lattice term. Above the transition however, the temperature dependence of $\Delta(T)$ is small, and it is perhaps not inconceivable that the tetrahedron is effectively regular with the splitting being derived solely by perturbation from a large lattice term originating from electronic charges external to the $[FeCl_4]^{2-}$ anion.

All the evidence suggests that there is still a further factor operating in $[NMe_4]_2FeCl_4$ which has not been previously considered. Although the unusually high magnetic moment has been interpreted in terms of a close-lying $3d^54s$ excited level,[3] this is thought to be a ^7S state at least 500 cm^{-1} above the ground state. This configuration would not contribute to the quadrupole splitting (being spherical in symmetry) so that the expression

$$\Delta(T) = \tfrac{2}{7}e^2Q\,\langle r^{-3}\rangle\,\frac{1 - e^{-\xi/kT}}{1 + e^{-\xi/kT} + e^{-\omega/kT}} \qquad (2)$$

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[3] R. J. H. Clark, R. S. Nyholm, and F. B. Taylor, *J. Chem. Soc.* (*A*), 1967, 1802.

[4] T. C. Gibb, N. N. Greenwood, and M. D. Sastry, *J.C.S. Dalton*, 1972, 1895.

would apply where $\omega \gg \xi$. For $\xi = 132$ cm^{-1} and $\omega = 500$ cm^{-1} the quadrupole splitting is only reduced by 4% at 240 K. The effect is far smaller than on the magnetic moment where the large increase in the number of unpaired electrons in the ^7S state is the major influence.

These difficulties in explaining the observed behaviour in terms of known phenomena have led us to examine the possibility that the explanation may lie in vibronic admixture of the $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ levels. A similar orbital scheme to that for tetrahedral d^6 configurations applies to an octahedral d^9 complex with three electrons in the E_g levels. Öpik and Pryce [5] and O'Brien [6] have shown that it is possible for lattice vibrations of E_g symmetry to mix the $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ levels in such octahedral complexes. Experimental evidence of these vibronic admixtures has been found.[7,8] In the present case of a high-spin tetrahedral iron(II) complex, lattice vibrations belonging to the E representation (normal modes of the type Q_2 and Q_3) will cause admixtures of the $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ states.[9]

If vibronic admixture occurs, the ground and excited state wave functions become

$$\phi_1 = \cos\theta|x^2 - y^2\rangle + \sin\theta|3z^2 - r^2\rangle \tag{3}$$

$$\phi_2 = \sin\theta|x^2 - y^2\rangle - \cos\theta|3z^2 - r^2\rangle \tag{4}$$

where the trigonometric functions of the argument θ are a convenient way of ensuring orthonormal wave functions. The elements of the electric field gradient tensor with the principal axes arbitrarily labelled are given for ϕ_1 by [10]

$$\begin{aligned} V_{11} &= 2(\cos^2\theta - \sin^2\theta) \\ V_{22} &= \sin^2\theta - \cos^2\theta + 2\sqrt{3}\cos\theta\sin\theta \\ V_{33} &= \sin^2\theta - \cos^2\theta - 2\sqrt{3}\cos\theta\sin\theta \\ V_{ij} &= 0\ (i \neq j) \end{aligned} \tag{5}$$

These values are for the instantaneous electric field gradient tensor and are expressed in units of $\frac{2}{7}e\langle r^{-3}\rangle$. The tensor for thermally populated excited states is given by

$$V_{jk}(T) = \frac{\sum_{\alpha}\langle\phi_\alpha|V_{jk}|\phi_\alpha\rangle \mathrm{e}^{-E_\alpha/kT}}{\sum_{\alpha}\mathrm{e}^{-E_\alpha/kT}} \tag{6}$$

from whence for the case of interest

$$\begin{aligned} V_{11}(T) &= 2(2\cos^2\theta - 1)\tanh(\xi/2kT) \\ V_{22}(T) &= (\sin^2\theta - \cos^2\theta + 2\sqrt{3}\cos\theta\sin\theta) \\ &\quad \tanh(\xi/2kT) \\ V_{33}(T) &= (\sin^2\theta - \cos^2\theta - 2\sqrt{3}\cos\theta\sin\theta) \\ &\quad \tanh(\xi/2kT) \end{aligned} \tag{7}$$

In the event that V_{11} corresponds to V_{zz} we have

$$V_{zz}(T) = (1 - 2\cos^2\theta)\tanh(\xi/2kT)V_{zz} \tag{8}$$

and

$$\eta = \frac{2\sqrt{3}\cos\theta\sin\theta}{(2\cos^2\theta - 1)} \tag{9}$$

where V_{zz} is the value for a pure $|3z^2 - r^2\rangle$ state (Note: in $[NMe_4]_2[FeCl_4]$ there is some evidence [2] for the ground state being $|3z^2 - r^2\rangle$ at low temperature in which case θ has a value of 90°). The quadrupole splitting is given by

$$\Delta(T) = \tfrac{1}{7}e^2Q\langle r^{-3}\rangle[V_{11}{}^2 + \tfrac{1}{3}(V_{22} - V_{33})^2]^{\frac{1}{2}} \tag{10}$$

which by substitution becomes

$$\Delta(T) = \tfrac{2}{7}e^2Q\langle r^{-3}\rangle\tanh(\xi/2kT) \tag{11}$$

This value is independent of the admixture of the E levels, as shown previously,[11] i.e. mixing of the $|3z^2 - r^2\rangle$ and $|x^2 - y^2\rangle$ states cannot be used to interpret our observations on a static model. With vibronic interaction, the value of θ fluctuates about a mean value so that $\overline{\cos^2\theta}$ and $\overline{\sin^2\theta}$ are finite, but $\overline{\cos\theta\sin\theta}$ is zero.[6] The measured quadrupole splitting is determined by the quasi-stationary electric field gradient [12] which will have the elements

$$\begin{aligned} \langle V_{11}(T)\rangle &= 2(2\overline{\cos^2\theta} - 1)\tanh(\xi/2kT) \\ \langle V_{22}(T)\rangle = \langle V_{33}(T)\rangle &= \\ (\overline{\sin^2\theta} &= \overline{\cos^2\theta})\tanh(\xi/2kT) \end{aligned} \tag{12}$$

The tensor now has an effective axial symmetry and

$$\langle\Delta(T)\rangle = \tfrac{2}{7}e^2Q\langle r^{-3}\rangle(2\cos^2\theta - 1)\tanh(\xi/2kT) \tag{13}$$

which is reduced from the static value by the parameter $(2\overline{\cos^2\theta} - 1)$.

Drawing a parallel with e.s.r. data for the d^9 octahedral configuration,[8] it seems likely that the degree of vibronic interaction will increase with rising temperature causing an apparent decrease in the value of $(2\overline{\cos^2\theta} - 1)$. This is consistent with the observed slope of the quadrupole splitting-temperature graph which does not show the expected asymptotic trend towards a zero value with rising temperature. Such vibronic interaction could also provide the basis for a change in the vibrational modes or a possible dynamic averaging of the tetragonal distortion above 239 K, resulting in the observed anomaly. However we have too little information about the compound to justify a more extensive interpretation of the data at the present time.

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