Polarized Mössbauer Absorption Studies on Single Crystals of Bis(η-cyclopentadienyl)iron

By **Terence C. Gibb**, Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

The orientation of the electric-field gradient (e.f.g.) tensor at the iron nucleus in [Fe(η-$C_5H_5)_2$] (ferrocene) has been determined by polarized Mössbauer measurements. The tensor is axially symmetric with the principal axis along the molecular axis. The molecules gradually rotate by *ca.* 20° in the vicinity of the λ transition at 164 K. A possible packing arrangement in the low-temperature phase has been devised which accounts for many of the observed properties.

THE molecular compound bis(η-cyclopentadienyl)iron, [Fe(η-$C_5H_5)_2$], commonly called ferrocene, has been extensively studied as the prototype of many derivatives with the same 'sandwich' structure. Nevertheless, its behaviour in the solid state is still not completely understood, and this paper reports some measurements by Mössbauer spectroscopy which throw a new light on the problem.

The *X*-ray crystal structure at room temperature is consistent with a $P2_1/a$ space group.[1] The centrosymmetric molecules have essentially D_{5d} molecular symmetry with the staggered or antiprismatic configuration, and pack in stacks along the crystallographic *c* axis. Specific-heat measurements[2] have shown an apparently second-order λ transition at 163.9 K, with an entropy change of $\Delta S = R \ln 1.89$ J K^{-1} mol^{-1}. Further *X*-ray measurements at 95, 135, 205, and 290 K gave no evidence[2] for a sharp discontinuity in the lattice parameters at the λ point, and it was suggested that the low-temperature phase consists of an ordered array of staggered molecules which suffers a partial degree of rotational disorder when heated through the λ point. Disorder is also indicated by neutron-diffraction data.[3] However, the room-temperature phase still contains a statistical predominance of staggered molecules.

Reorientation of the C_5H_5 rings has been observed in the n.m.r. spectrum.[4,5] The activation energy is low, and the correlation time of 10^{-6} s at 78 K increases rapidly to *ca.* 10^{-10} s at 170 K. However, this process is clearly a co-operative jump–rotation of adjacent rings, rather than free rotation. Electron-diffraction measurements in the gas phase[6] suggest that the equilibrium configuration of the free molecule is eclipsed, but with a very low energy barrier to internal rotation.

There have been many measurements of the infrared and Raman spectra of solid ferrocene. The most recent assignments of the i.r.[7] and Raman spectra[8-10] are in reasonable agreement. On cooling from 185 to 165 K, the only significant changes[8] in the Raman spectrum are a gradual shift in the librational modes from 71 to 64 cm^{-1}, and the introduction of some weak lines consistent with a breakdown in the selection rules in the ordered structure. Two molecular inter-ring i.r.-inactive modes at 388 and 312 cm^{-1} were observed[11] to become gradually active between 180 and 140 K, and have been taken to indicate an ordered lattice with non-centrosymmetric sites. The persistence of these bands above 164 K indicates an initial retention of some short-range order in the disordered phase. This is not recorded as sensitively by the specific-heat data which are influenced more by the long-range order of the crystal. However, the vibrational data give no positive indications as to whether the staggered configuration is retained in the ordered phase, or is replaced by an eclipsed configuration.[11]

The crystal structure was originally thought to retain the $P2_1/a$ space group below the λ point, but it is now known to become triclinic with only very small changes in the unit-cell parameters.[8,12,13] A detailed study of the *X*-ray powder pattern was published during the course of the present work, and gives evidence for a small discontinuity in the lattice parameters at 164 K as if the transition were of first order.[13] The coefficients of thermal expansion indicate that there is a significant contraction along the *c* axis, but an expansion along the orthogonal *a′* axis on cooling through the λ point. It appears that two effects may be operative: an order–disorder process which produces the continuous variation in cell parameters between 130 and 220 K, and a sudden molecular reorientation process which causes the discontinuity at 164 K.

When large crystals of ferrocene are cooled below the λ point they undergo a violent disintegration into a powder. Although originally associated with the λ transition itself, it is now clear[14] that this is a separate phenomenon which takes place somewhere in the range 125—108 K according to the rate of cooling, and probably results from a disintegration of a multi-domain structure into single-domain crystallites.

The ^{57}Fe Mössbauer spectrum of ferrocene comprises

---

[1] J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Cryst.*, 1956, **9**, 373.

[2] J. W. Edwards, G. L. Kington, and R. Mason, *Trans. Faraday Soc.*, 1960, **56**, 660.

[3] B. T. M. Willis, A.E.R.E. Report (Harwell), R3708, 1961.

[4] C. H. Holm and J. A. Ibers, *J. Chem. Phys.*, 1959, **30**, 885.

[5] L. N. Mulay and A. Attalla, *J. Amer. Chem. Soc.*, 1963, **85**, 702.

[6] A. Haaland and J. Nilsson, *Chem. Comm.*, 1968, 88.

[7] I. J. Hyams, *Spectrochim. Acta*, 1973, **A29**, 839.

[8] I. J. Hyams, *Chem. Phys. Letters*, 1973, **18**, 399.

[9] J. Bodenheimer, E. Loewenthal, and W. Low, *Chem. Phys. Letters*, 1969, **3**, 715.

[10] R. T. Bailey, *Spectrochim. Acta*, 1971, **A27**, 199.

[11] I. J. Hyams and A. Ron, *J. Chem. Phys.*, 1973, **59**, 3027.

[12] J. F. Berar and G. Calvarin, *Compt. rend.*, 1973, **C277**, 1005.

[13] G. Calvarin and J. F. Berar, *J. Appl. Crystallography*, 1975, **8**, 380.

[14] J. S. Bodenheimer and W. Low, *Phys. Letters*, 1971, **A36**, 253.

a quadrupole doublet with a separation of *ca.* 2.4 mm s^{-1} which is almost independent of temperature.[15] Collins [16] showed that the quadrupole coupling constant was positive in sign, and could be interpreted in terms of molecular-orbital (m.o.) theory with the implication that the principal axis of the electric-field gradient (e.f.g.) tensor lies along the molecular axis and that the asymmetry parameter η is zero (the present work on single crystals confirms this). A previous single-crystal measurement [17] was shown to be consistent with this interpretation, but did not constitute a direct measurement of the orientation of the tensor.

In view of the many questions still unanswered about the structure of solid ferrocene, it was decided to measure the orientation of the e.f.g. tensor at the ^{57}Fe nucleus in the monoclinic phase, and to investigate the λ transition by Mössbauer spectroscopy.

RESULTS AND DISCUSSION

The Electric-field Gradient Tensor.—The cross-section for Mössbauer absorption in a single crystal shows a polarization dependence which causes the absorption intensities of hyperfine components to saturate with absorber thickness in a manner very different to that found in an unpolarized isotropic polycrystalline sample.[18] This has led to the development of a new method of accurately determining the orientation of an e.f.g. tensor.[19] The method uses a polarized source of ^{57}Co in iron metal magnetized in an external field, and has been previously applied to $Fe[NH_4]_2[SO_4]_2 \cdot 6H_2O$,[19] $Na_2[Fe(CN)_5(NO)] \cdot 2H_2O$,[20] and $FeCl_2 \cdot 4H_2O$.[21] The principles and experimental techniques have already been given in detail in these earlier papers to which the reader is referred. The absorption cross-section of the i'th hyperfine component is expressed by a density matrix which can be made diagonal if the direction of observation is normal or parallel to an even-fold rotation axis. The incident radiation can then be considered as two components propagating independently through the crystal and polarized parallel to the basis polarizations, s and t, in which the matrix is diagonal.

The derivation of the density matrix elements for the monoclinic phase of ferrocene ($P2_1/a$) follows the principles already given.[22] The Cartesian axis system a,b,c' is chosen where a and b are the crystallographic axes. Crystals of ferrocene of a suitable size for the experiment can be grown on the 001 (ab) plane. The direction of observation is therefore taken to be normal to the 001 plane as the k axis of an s,t,k Cartesian system. There are two equivalent crystallographic sites related by a 180° rotation about the b axis. The e.f.g. tensor at site 1 has an axis system x_1,y_1,z_1 which is related to a,b,c' by the Euler transform $D(\alpha,\beta,\gamma)$, where α is an anticlockwise rotation about c', followed by an anticlockwise rotation β about the new b axis, and finally an anticlockwise rotation γ about the new c' axis.

The density matrix for the combined sites can be shown to be diagonal if the s axis is parallel to a, and the t axis is parallel to b, so that equations (1)—(3) are

$$\rho_{ss} = \tfrac{1}{2} \pm \tfrac{1}{4}\left(\frac{3}{3+\eta^2}\right)^{\frac{1}{2}} [1 - 3\sin^2\alpha\sin^2\beta + \eta\cos 2\gamma\,(\cos^2\alpha - \sin^2\alpha\cos^2\beta)] \pm \left(\frac{\eta}{4}\right)\left(\frac{3}{3+\eta^2}\right)^{\frac{1}{2}} \sin 2\alpha\cos\beta\sin 2\gamma \quad (1)$$

$$\rho_{tt} = \tfrac{1}{2} \pm \tfrac{1}{4}\left(\frac{3}{3+\eta^2}\right)^{\frac{1}{2}} [1 - 3\cos^2\alpha\sin^2\beta + \eta\cos 2\gamma\,(\sin^2\alpha - \cos^2\alpha\cos^2\beta)] \mp \left(\frac{\eta}{4}\right)\left(\frac{3}{3+\eta^2}\right)^{\frac{1}{2}} \sin 2\alpha\cos\beta\sin 2\gamma \quad (2)$$

$$\rho_{st} = \rho_{ts} = 0 \quad (3)$$

obtained, where the upper sign refers to the $\pm\frac{1}{2}\rightarrow\pm\frac{3}{2}$ quadrupole transition (π) and the lower sign to the $\pm\frac{1}{2}\rightarrow\pm\frac{1}{2}$ transition (σ). Thus ρ_{ss} and ρ_{tt} are dependent only on η and the angles α, β, and γ. The possible influences of disorder are discussed later. For an absorber containing n atoms cm^{-2} of the resonant element whose isotopic abundance of the Mössbauer nuclide is a, resonant cross-section is σ_0, and recoilless fraction is f, the effective cross-section for absorption is $C_A = anf\sigma_0$. The area ratio in the quadrupole spectrum recorded using an unpolarized source will be given by equation (4),[19] where $K(x) = x\exp(-x/2)[J_0(ix/2) + J_1(ix/2)]$.

$$R_1 = \frac{I_\pi}{I_\sigma} = \frac{K(\rho_{ss}{}^{\pi}C_A) + K(\rho_{tt}{}^{\pi}C_A)}{K(\rho_{ss}{}^{\sigma}C_A) + K(\rho_{tt}{}^{\sigma}C_A)} \quad (4)$$

If the source is polarized with the axis of polarization parallel to either the s or t axis of the absorber, then each emission line is completely polarized with respect to the basis polarizations. The ratio of the π and σ intensities for absorption of a hyperfine component polarized parallel to s (along the a axis) will be as in equation (5). Similarly for the component polarized

$$R_2 = I_a/I_b = K(\rho_{ss}{}^{\pi}C_A)/K(\rho_{ss}{}^{\sigma}C_A) \quad (5)$$

parallel to t (along the b axis), equation (6) is obtained.

$$R_3 = I_c/I_d = K(\rho_{tt}{}^{\pi}C_A)/K(\rho_{tt}{}^{\sigma}C_A) \quad (6)$$

By combining the line intensities between pairs of source emission lines it is possible to obtain equations (7) and (8), where x is the relative intensity of the incident emission lines.

$$R_4 = xI_a/I_c = K(\rho_{ss}{}^{\pi}C_A)/K(\rho_{tt}{}^{\pi}C_A) \quad (7)$$

$$R_5 = xI_b/I_d = K(\rho_{ss}{}^{\sigma}C_A)/K(\rho_{tt}{}^{\sigma}C_A) \quad (8)$$

---

[15] G. K. Wertheim and R. H. Herber, *J. Chem. Phys.*, 1963, **38**, 2106.

[16] R. L. Collins, *J. Chem. Phys.*, 1965, **42**, 1072.

[17] J. T. Dehn and L. N. Mulay, *J. Inorg. Nuclear Chem.*, 1969, **31**, 3103.

[18] R. M. Housley, R. W. Grant, and U. Gonser, *Phys. Rev.*, 1969, **178**, 514.

[19] T. C. Gibb, *J. Phys. C*, 1975, **8**, 229.

[20] T. C. Gibb, *Chem. Phys. Letters*, 1975, **30**, 137.

[21] T. C. Gibb, *Chem. Phys.*, 1975, **7**, 449.

[22] T. C. Gibb, *J. Phys. C*, 1974, **7**, 1001.

In the present instance it is possible to record the absorption spectrum of an 001 crystal with the source polarization direction parallel to a and b in turn. This gives sufficient data to determine $R_1 - R_5$, and with a value for C_A these can be used to determine α, β, γ, and η. The value of f which is unknown can be obtained with sufficient accuracy from the dependence of the experimental linewidth on absorber thickness.[22]

A number of 001 crystals were grown by recrystallization from absolute alcohol and identified optically. The spectrum at 298 K of a crystal containing 18.3 mg cm^{-2} of iron obtained with the direction of observation along c' and using an unpolarized ^{57}Co–Rh source gave an area ratio of $R_1 = 0.611 \pm 0.036$. This crystal was too small, however, for use in the polarized-source experiment, and a matrix of 15 crystals with thicknesses of 23—28 mg cm^{-2} of iron was made. This gave a better quality spectrum with $R_1 = 0.632 \pm 0.022$, a quadrupole splitting of $\Delta = 2.378 \pm 0.004$ mm s^{-1}, a chemical isomer shift of $\delta = 0.441 \pm 0.005$ mm s^{-1} (with respect to iron metal at the same temperature), and experimental linewidths of $\Gamma_\pi = 0.221 \pm 0.006$ and $\Gamma_\sigma = 0.228 \pm 0.004$ mm s^{-1}. The experimental linewidths of spectra from both single crystals and polycrystalline absorbers were used [22] to obtain an approximate estimate of 0.07 for f along the c' axis in the single crystal (from symmetry considerations the value is identical at both sites). The individual uncertainties in n and f for the multiple-crystal matrix are reduced by mutual compensation in the estimated value of C_A. In any event, the saturation effects were not very large, so that any error introduced by wrongly estimating C_A will be small.

The Mössbauer spectra of the crystal matrix using the polarized source magnetized parallel and perpendicular to the b axis (along t and s respectively) are shown in Figure 1. The area ratios $R_1 - R_5$ were obtained by computer analysis. The calculation was constrained to utilize one parameter each for the magnetic hyperfine splitting and quadrupole splitting. A common linewidth was specified, and appropriate pairs of lines were constrained to have equal intensities. Although several pairs of lines are strongly overlapping, in all cases these represent different emission polarizations so that the total absorption intensity is additive. The final values were $R_2 = 0.605 \pm 0.060$, $R_3 = 0.666 \pm 0.063$, $R_4 = 0.948 \pm 0.117$, and $R_5 = 1.054 \pm 0.072$. The errors in these parameters are somewhat higher than in similar measurements on other compounds because of the low value of f, but corresponding calculated values are sufficiently sensitive to changes in the values of α, β, and γ for a solution to be clearly defined. Ignoring equivalent solutions for the same e.f.g. tensor, there are four inter-related solutions corresponding to an ambiguity between sites 1 and 2, and an ambiguity in the direction of observation. With the assumption that e^2qQ is positive (established by Collins [16]) and that $f = 0.07$, $\sigma_0 = 2.57 \times 10^{-18}$ cm^2, a solution can be obtained ($\alpha = 47 \pm 2$, $\beta = 90 \pm 5$, $\gamma = 0°$, $\eta = 0$) which gives the calculated parameters $R_1 = 0.632$, $R_2 = 0.612$, $R_3 = 0.668$, $R_4 = 0.945$, and $R_5 = 1.039$.

The orientation of the molecule as specified by the centre of mass of the C_5H_5 ring [1] corresponds to $\alpha = 45°$ and $\beta = 87°$. The principal axis of the e.f.g. tensor therefore lies either parallel or perpendicular to the molecular axis. It is not possible to eliminate the latter possibility because the molecular axis at site 1 is orientated at exactly 90° to that at site 2, although it must be considered unlikely. It was also found that some solutions to the data exist in which η has a small finite value, but only if γ is very close to 45°. The magnetic-perturbation data give no evidence for a large value of η,[16] and the narrow restriction on γ suggests that this possibility can be disregarded.

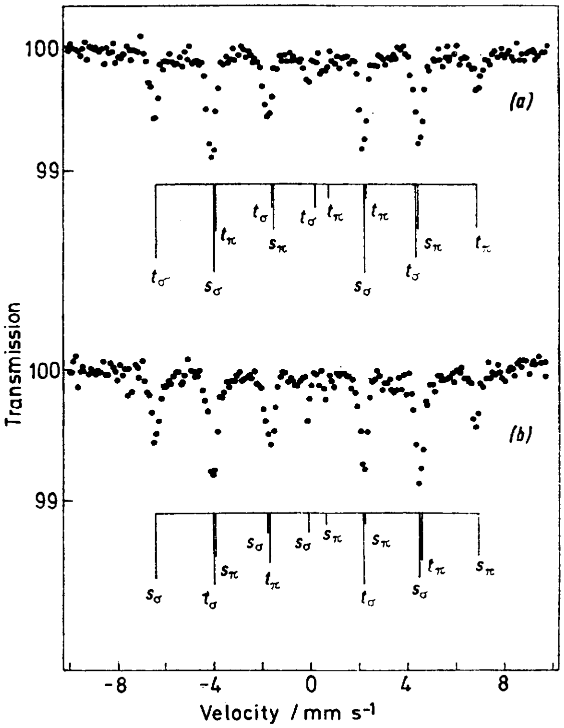

FIGURE 1 Mössbauer spectra of a matrix of single crystals of ferrocene obtained with a polarized source magnetized (a) parallel to the b axis and (b) perpendicular to the b axis, and observed along the c' axis. The absorption lines are identified as being the π or σ transitions in the absorber with polarization parallel to the s or t axis

The results obtained are not expected to be significantly influenced by the presence of the disorder. In any case the disorder does not appear to affect the orientation of the molecular axis, and any rotational disorder of the C_5H_5 rings is not expected to affect the Mössbauer spectrum. It can therefore be concluded that the e.f.g. tensor has effectively axial symmetry, and that the principal axis is also the molecular axis in accord with the m.o. description.[16]

The Lambda Transition.—The Mössbauer spectrum of a polycrystalline sample of ferrocene was recorded at

11 temperatures in the range 87—297 K using an unpolarized ^{57}Co–Rh source. For experimental reasons, the thickness of the sample was not accurately controlled, but the measurements were recorded in a continuous series and are internally self-consistent. Each spectrum was computed with two unconstrained Lorentzian curves, and the chemical isomer shift (with respect to iron metal at 297 K), quadrupole splitting, and relative area of the absorption intensity were determined. The data are illustrated by the circles in Figures 2 and 3. The triangles are for single-crystal data which are referred to later. The chemical isomer shift (Figure 2) shows the increase with decrease in temperature characteristic of the second-order Doppler shift, but the quadrupole splitting is almost independent of temperature. In neither case is there any obvious change at the λ transition. The logarithm of the spectrum area (Figure 3) shows a linear behaviour at temperatures above the λ transition, but a significant deviation occurs below this temperature. This indicates a substantial modification in the lattice characteristics of the solid at the order–disorder transition.

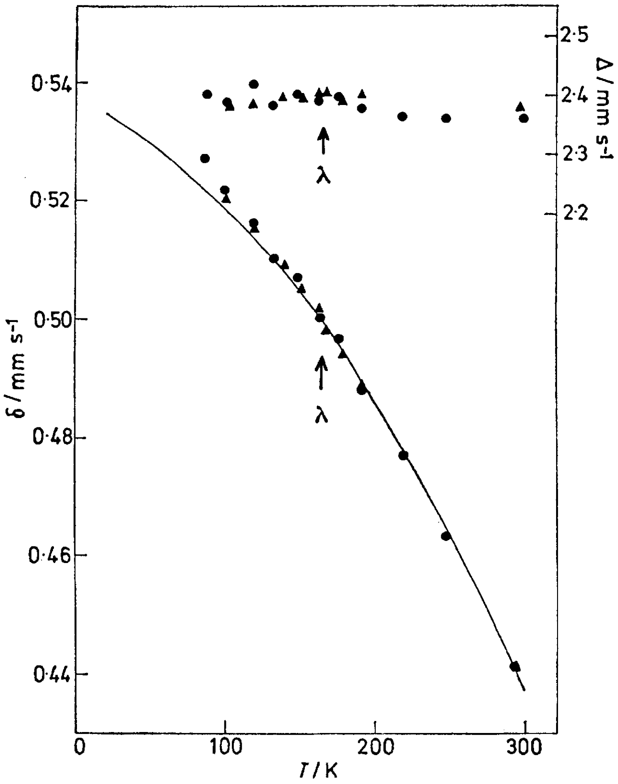

FIGURE 2 The chemical isomer shift (δ) and quadrupole splitting (Δ) of ferrocene as a function of temperature (T): (●) data from a polycrystalline sample; (▲), data from the crystal matrix

The lattice dynamics of molecular solids are only poorly understood. Nevertheless it is possible to qualitatively explain the data. The second-order Doppler shift, $\delta E/E_\gamma$, is related to the mean-square velocity, $\langle v^2\rangle$, by equation (9), where c is the velocity

$$\delta E/E_\gamma = -\langle v^2\rangle/2c^2 \qquad (9)$$

of light and E_γ is the energy of the gamma ray. Similarly the recoilless fraction f is related to the mean-square vibrational amplitude by equation (10). In general one

$$f = \exp[-E_\gamma^2\langle x^2\rangle/(\hbar c)^2] \qquad (10)$$

can say that $\langle x^2\rangle$ is weighted towards lower frequencies than $\langle v^2\rangle$, so that in a molecular solid f is influenced strongly by the intermolecular vibrations, while $\delta E/E_\gamma$ is more sensitive to the intramolecular vibrations. It is therefore not surprising that the chemical isomer shift is not strongly influenced by the phase transition.

It is interesting to apply a simple two-frequency model for the vibrations of the resonant atom in the manner devised by Hazony.[23] Following his nomenclature, low and high frequencies are signified by $k\theta_l = \hbar\omega_l$ and $k\theta_h = \hbar\omega_h$ respectively. At intermediate temperatures where $\theta_l < T < \theta_h$ it is possible to show that equations (11) and (12) are applicable where $\eta_l = [\exp(\theta_l/T) - 1]^{-1}$,

$$\mathrm{d}\ln f/\mathrm{d}T \approx -(kE_\gamma^2/M'c^2)[1/(k\theta_l)^2] \qquad (11)$$

$$\delta E/E_\gamma = -\frac{3}{2}E_\gamma[(k\theta_l/M'c^2)(\tfrac{1}{2} + \eta_l) + (k\theta_h/M''c^2)(\tfrac{1}{2} + \eta_h)] \qquad (12)$$

M' is the molecular mass, M is the mass of the resonant nucleus, and $M'' = M'M/(M' - M)$. If the area of the spectrum is directly proportional to the recoilless fraction (*i.e.* saturation effects are small, which appears to be the case above the phase transition because of the low values of the recoilless fraction), then $\ln f$ should depend

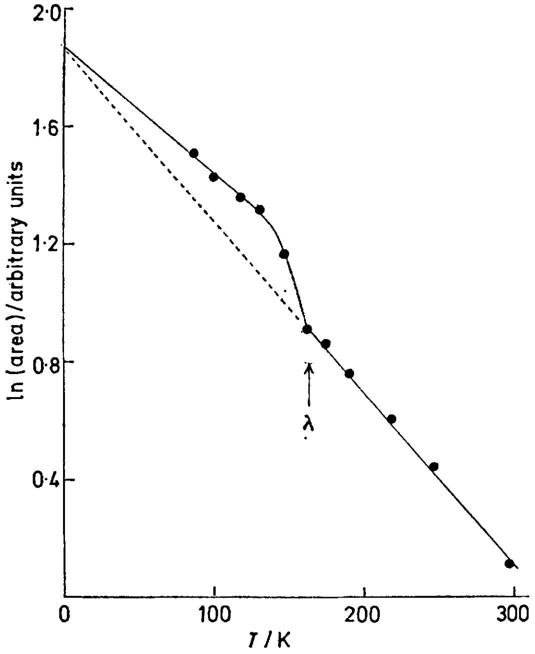

FIGURE 3 Temperature dependence of the spectrum area of a polycrystalline sample of ferrocene

---

[23] Y. Hazony, *J. Chem. Phys.*, 1966, **45**, 2664.

linearly on temperature. Figure 3 shows that this is the case. The gradient of the line gives a value for θ_l of 48 K. If the effective lattice frequency changes below the lambda transition there should be a change in gradient, but the extrapolated origin of the line on a logarithmic plot will be almost identical. On this basis the full line below 130 K has been drawn to correspond to a value for θ_l of 58 K. These values make an interesting comparison with the known librational frequencies[8] at *ca.* 68 cm^{-1} (*ca.* 98 K). There is a progressive decrease in the recoilless fraction from *ca.* 20 degrees below and ceasing abruptly at the λ point where long-range order is destroyed.

The value of $\theta_l = 48$ K was incorporated into the equation for $\delta E/E_\gamma$ to obtain a value for θ_h which would fit the chemical-isomer-shift data above the λ point. The full line in Figure 2 corresponds to $\theta_h = 700$ K. It was not possible to find a value for θ_h which also fitted the low-temperature data, and it seems that the deviation below the λ transition is a real phenomenon.

In an attempt to obtain more information about the λ transition, the matrix of single crystals described earlier was examined at seven temperatures below 190 K. The quadrupole-splitting and chemical-isomer-shift values obtained were fully self-consistent with the polycrystalline data, and are therefore included in Figure 2. The temperature dependence of the spectrum area (which should be a function of f along the c' axis) also showed an anomalous increase near the λ transition, but was not studied over a large enough temperature range for a detailed discussion.

The most interesting observation was a significant increase in the area ratio I_π/I_σ between 185 and 145 K. This is shown in Figure 4. The change begins well above the λ point and is therefore not caused solely by the increased saturation effect as f increases below the λ point. The dependence of the area ratio on temperature (assuming no change in structure but an increase in recoilless fraction) can be approximately estimated by taking the value of $f = 0.07$ at 297 K and scaling it in accord with Figure 3. This assumes that the value of $\langle x^2 \rangle$ along c' is closely related to the averaged value $\overline{\langle x^2 \rangle}$ which may not be the case, but the errors introduced should be small. For example, f increases to *ca.* 0.15 at 164 K, which with $\alpha = 45°$ and $\beta = 90°$ leads to an area ratio of $I_\pi/I_\sigma = 0.668$. Agreement is good from room temperature down to 190 K. However, it is not possible to interpret the data at lower temperatures solely by increasing the value of f along the c' axis, and it seems necessary to invoke a reorientation of the e.f.g. tensor. This can be taken to signify a concomitant rotation of the molecular axis. A change in the angle α produces little effect, but a change in β can increase the area ratio. Calculated values for $\beta = 85$, 80, 75, and 70° are included in Figure 4.

The only viable explanation seems to be that the molecular axis rotates out of the *ab* plane. Crystal disintegration[14] is not responsible as this was clearly detected in the Mössbauer spectra below 119 K, and in any case the rotation commences well above the transition temperature. The rotation can be estimated at $20 \pm 2°$ if all molecules rotate equally. If some of the molecules do not rotate, then a much greater movement is implied for the remainder, and this seems less likely. The rotation takes place gradually with the order–disorder reorientation, and is not associated with a discontinuity at the λ transition. It is possible that the latter is produced by a reorientation of the C_5H_5 rings alone.

The close similarity in the lattice parameters of the monoclinic (disordered) and triclinic (ordered) forms of ferrocene[13] suggests that the packing of the molecules is similar in the two structures. The new evidence implies that there is a rotation of the molecular axis out of the *ab* plane by 20°, and it is interesting to examine how this can take place. To this end a program was written to calculate the H–H distances between molecules for different orientations in an idealized structure. The monoclinic cell parameters of $a = 10.561$, $b = 7.597$, $c = 5.952$ Å, and $\beta = 121°$ were used, together with interatomic distances of 3.32 Å for the ring–ring separation, 1.40 Å for C–C, and 1.08 Å for the C–H bond distance. The molecules were assumed to be regular, and both staggered (D_{5d}) and eclipsed (D_{5h}) configurations were considered. The $P2_1/a$ symmetry restrictions were assumed for the site inter-relation.

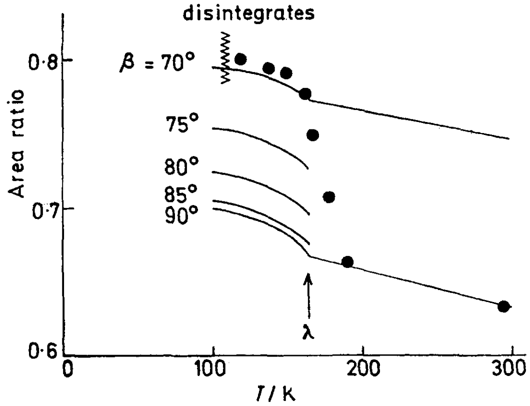

FIGURE 4 Temperature dependence of the area ratio, I_π/I_σ, in a crystal matrix of ferrocene observed along the c' axis. The full lines show the predicted behaviour for different values of the angle β

The best packing arrangement which could be found with the molecular axis close to the *ab* plane corresponded almost exactly with the established monoclinic structure, and this is illustrated in Figure 5. The molecular axis is defined by $\alpha = 45°$ and $\beta = 87°$. The shortest calculated distances were two of 2.33 Å with adjacent molecules at $(\frac{1}{2},\frac{1}{2},1)$ and two at 2.34 Å with molecules along the b axis. The nearest contact with molecules along the c axis was 2.49 Å. The van der Waals distance for H–H interaction is normally considered to be *ca.* 2.3—2.5 Å, and, bearing in mind that the predicted structure is idealized, the H–H distances are clearly all non-bonding. The larger separation along the *c* axis is probably a result of the disorder.

An attempt to find a packing arrangement for the ordered phase gave encouraging results. One possible idealized arrangement is shown in Figure 6 with the molecular axis defined by $\alpha = 46°$ and $\beta = 70°$. A rotation by 20° out of the *ab* plane seems to correspond to a local maximum in the shortest H–H distances, and agrees well with the prediction made from the Mössbauer data. The shortest H–H distances are four of 2.28 Å between molecules along the *c* axis. This decrease in separation along the *c* axis is perhaps a not unexpected consequence of the removal of the disorder. The next-nearest distances are at 2.36 Å with molecules at $(\frac{1}{2},\frac{1}{2},1)$. Although the non-bonding distances are now apparently shorter, it must be remembered that three important factors have been omitted: (*a*) the unit cell has distorted; (*b*) the molecule may be slightly distorted; and (*c*) configurations intermediate between staggered and eclipsed forms have not been considered. This latter factor is probably very important, especially as the molecular site is no longer centrosymmetric. Moreover, the calculations show that it would be much easier to accommodate an eclipsed molecule in the lattice when $\beta = 70°$ than when $\beta = 87°$, which would facilitate the rapid reorientation which takes place at low temperatures. It should also be noted that a nearly eclipsed configuration is favoured in most ferrocene derivatives.[24]

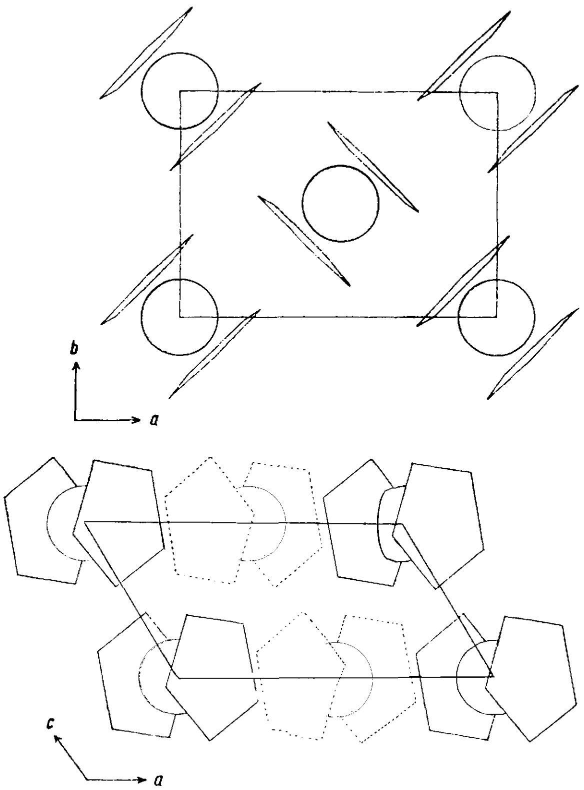

FIGURE 5 Projections on the *ac* and *ab* planes in the unit cell of the idealized structure of ferrocene in the monoclinic phase. The sides of the pentagons are drawn between the hydrogen-atom positions. The orientation of the molecule corresponds to $\alpha = 45°$ and $\beta = 87°$

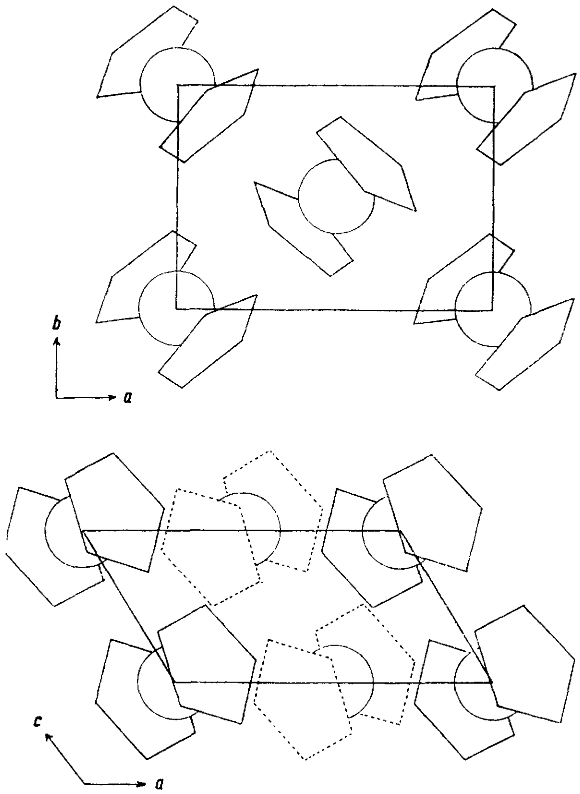

FIGURE 6 Projections on the *ac* and *ab* planes in the unit cell of a possible packing arrangement for ferrocene in the triclinic phase. The orientation of the molecule corresponds to $\alpha = 46°$ and $\beta = 70°$. The rings are shown in a staggered configuration, but an eclipsed or partially eclipsed configuration might also be accommodated in a basically similar arrangement

In view of the constraints placed on the calculation, it is very encouraging to find such good agreement with observation. A reorientation of this magnitude had not been previously suspected. Although it seems highly probable that the molecular packing at low temperatures resembles that shown in Figure 6, it would be unwise to assume that the configuration of the molecules is still staggered. It appears that there is a strong case for attempting an *X*-ray structure determination on the triclinic phase.

[5/2375 *Received, 8th December,* 1975]

---

[24] A. P. Krukonis, J. Silverman, and N. F. Yamoni, *Acta Cryst.*, 1972, **B28**, 987.