

## Further Studies on the Spin Cross-over Phenomenon in Di-isothiocyanatobis(1,10-phenanthroline)iron(II)

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Some inconsistencies in the results of earlier Mössbauer spectroscopic and magnetic susceptibility measurements on  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  (phen = 1,10-phenanthroline) demanded a systematic reinvestigation of this system. We have prepared the complex by two different methods: precipitation in methanol (A) and extraction from  $[\text{Fe}(\text{phen})_3][\text{NCS}]_2$  with acetone (B). The two samples (A and B) differ in crystal size and quality, which markedly influences the spin-transition behaviour. Mössbauer and magnetic susceptibility measurements down to ca. 4 K show that spin conversion is gradual in sample A but rather abrupt in sample B. This is supported by differential thermal analysis measurements. There is 'residual paramagnetism' of ca. 12% in sample A, but none in sample B. A sharp fall in the Mössbauer resonance line width and a distinct irregularity in the quadrupole splitting of the high-spin state near  $T_c$  suggests that a structural change occurs as the system undergoes spin cross-over. Temperature-dependent changes in the X-ray diffraction patterns support this suggestion.

THE well documented<sup>1</sup> abrupt spin cross-over  $^1A_1(O_h) \rightleftharpoons ^5T_2(O_h) \uparrow$  in  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  (phen = 1,10-phenanthroline) has previously been extensively studied by Mössbauer,<sup>2,3</sup> magnetic susceptibility,<sup>1-4</sup> i.r.,<sup>2,5,6</sup> far-i.r.,<sup>7-9</sup> u.v.-visible,<sup>2</sup> n.m.r.,<sup>3</sup> heat capacity,<sup>9,10</sup> and X-ray<sup>1,2</sup> techniques. Although the spin transition has been well established, the correlation between the results from various techniques has not always been very satisfactory. In particular, the 'residual paramagnetism' in this system strongly depends on the method of preparation,<sup>2-4</sup> although none of the techniques, except for magnetic susceptibility, has revealed any apparent differences between the samples prepared by different methods. Such inconsistencies in the previous results prompted us to undertake a thorough recharacterization of the system by Mössbauer spectroscopy and other complementary techniques. Some of our initial results have been communicated earlier.<sup>11</sup> Here we report our detailed observations on  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  prepared by two different methods.

### EXPERIMENTAL

The compound  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  was prepared by the following two methods.

**Method A (ref. 12).**—Moisture-free methanol solutions of potassium thiocyanate  $\text{K}[\text{SCN}]$  (0.008 mol) and hydrated iron(II) chloride  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  (0.004 mol) were stirred until the reaction to iron(II) thiocyanate,  $\text{Fe}[\text{SCN}]_2$ , was complete. The precipitated potassium chloride was filtered off. A stoichiometric amount of 1,10-phenanthroline monohydrate in methanol was added dropwise to the well stirred filtrate containing  $\text{Fe}^{2+}$  and  $\text{SCN}^-$  ions. The pink-violet precipitate of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  was filtered off, washed several times with methanol, and dried *in vacuo* over phosphorus pentoxide. All operations were carried out under nitrogen in a dry box.

**Method B (ref. 13).**—In this case  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  was prepared by extracting a phenanthroline group from  $[\text{Fe}(\text{phen})_3][\text{NCS}]_2 \cdot \text{H}_2\text{O}$  in a Soxhlet apparatus using acetone. The extraction was carried out over a period of 3 weeks under an argon atmosphere. The dark blue-violet crystals

thus obtained were dried *in vacuo* over phosphorus pentoxide.

**Sample A.** Found: C, 58.2; H, 3.0; Fe, 10.3; N, 15.9%. **Sample B.** Found: C, 58.4; H, 2.8; Fe, 10.6; N, 15.7%. Calc. for  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ : C, 58.7; H, 3.1; Fe, 10.5; N, 15.8%.

The compound  $[\text{Fe}(\text{phen})_3][\text{NCS}]_2 \cdot \text{H}_2\text{O}$  was prepared by adding a saturated aqueous solution of potassium thiocyanate ( $\text{K}[\text{SCN}]$ ) to a well stirred aqueous solution of iron(II) ammonium sulphate and 1,10-phenanthroline monohydrate (in stoichiometric amounts). The precipitate was dried *in vacuo* over  $\text{P}_2\text{O}_5$ . Elemental analysis showed that it was the required product.

X-Ray powder photographs at 293 K of the two samples were identical, but distinctly different from that of  $[\text{Fe}(\text{phen})_3][\text{NCS}]_2 \cdot \text{H}_2\text{O}$ . Infrared spectra recorded at room temperature in the range 550—4 000  $\text{cm}^{-1}$  did not show any apparent differences between the samples A and B. The only significant difference between the two samples is their crystal size and colour. Comparison of the particle sizes under a microscope shows that sample A is an extremely fine powder whereas the particles of sample B are about five times bigger on average.

The Mössbauer spectra were recorded in transmission geometry, using a Kankeleit drive,<sup>14</sup> in the constant acceleration mode. The source, 20 mCi  $^{57}\text{Co}$  in Rh (provided by the Radiochemical Centre, Amersham), was held at 293 K. The absorber thickness was ca. 0.1 mg  $^{57}\text{Fe}$   $\text{cm}^{-2}$ . Samples were sealed in poly(methyl methacrylate) containers under  $\text{N}_2$ . A standard helium cryostat with a variable-temperature facility was used for the measurements. The temperature stability in the cross-over region is considered to be  $< \pm 0.3$  K. The spectra were fitted to two quadrupole doublets by a least-squares iteration method using a PDP 11/34 computer.

The magnetic measurements (from 4.2—300 K) on sample A were carried out at the Kernforschungszentrum Karlsruhe using a Faraday balance. The magnetic susceptibility as a function of temperature of sample B was measured in our laboratory using a Foner magnetometer (temperature stability  $< \pm 0.04$  K).

The temperature-dependent (77—300 K) X-ray measurements were carried out using a Siemens counter diffractometer equipped with a flow-type cryostat.  $\text{Cu-K}_\alpha$  Radiation ( $\lambda = 1.541 \text{ \AA}$ ) was used for all the measurements. The

† Nomenclature for the approximation of  $O_h$  symmetry.

‡ Throughout this paper: 1 Ci =  $3.7 \times 10^{10} \text{ s}^{-1}$ .

TABLE 1

Isomer shift ( $\delta$ ) (relative to iron foil), quadrupole splitting ( $\Delta$ ), line width ( $\Gamma/2$ ), and area fraction ( $A$ ) from the temperature-dependent Mössbauer spectra of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , sample A\*

| $T/K$ | High-spin doublet |                                |            | $A(\%)$    | Low-spin doublet |                                |            | $A(\%)$    |
|-------|-------------------|--------------------------------|------------|------------|------------------|--------------------------------|------------|------------|
|       | $\delta$          | $\Delta$<br>mm s <sup>-1</sup> | $\Gamma/2$ |            | $\delta$         | $\Delta$<br>mm s <sup>-1</sup> | $\Gamma/2$ |            |
| 300   | 1.007(8)          | 2.706(15)                      | 0.175(11)  | 94.8 ± 5.0 | 0.327(150)       | 0.300(122)                     | 0.174(231) | 5.2 ± 3.7  |
| 280   | 1.019(7)          | 2.776(15)                      | 0.155(8)   | 92.0 ± 3.8 | 0.339(69)        | 0.320(55)                      | 0.158(99)  | 8.0 ± 2.8  |
| 260   | 1.029(7)          | 2.846(15)                      | 0.151(7)   | 89.5 ± 3.4 | 0.348(37)        | 0.386(31)                      | 0.134(48)  | 10.5 ± 2.3 |
| 240   | 1.039(7)          | 2.901(15)                      | 0.161(7)   | 87.6 ± 3.2 | 0.389(42)        | 0.327(34)                      | 0.173(63)  | 12.4 ± 2.4 |
| 220   | 1.071(6)          | 3.016(16)                      | 0.155(6)   | 83.8 ± 2.4 | 0.401(21)        | 0.358(17)                      | 0.152(28)  | 16.2 ± 1.7 |
| 200   | 1.082(6)          | 3.068(16)                      | 0.154(5)   | 76.8 ± 1.8 | 0.413(10)        | 0.350(8)                       | 0.144(13)  | 23.2 ± 1.2 |
| 190   | 1.093(6)          | 3.089(16)                      | 0.155(6)   | 69.4 ± 2.0 | 0.431(7)         | 0.358(6)                       | 0.131(10)  | 30.6 ± 1.3 |
| 188   | 1.089(6)          | 3.093(16)                      | 0.155(6)   | 65.3 ± 1.8 | 0.432(6)         | 0.354(5)                       | 0.137(8)   | 34.7 ± 1.2 |
| 186   | 1.096(6)          | 3.096(16)                      | 0.161(6)   | 60.8 ± 1.8 | 0.433(6)         | 0.353(5)                       | 0.142(8)   | 39.2 ± 1.2 |
| 184   | 1.099(6)          | 3.114(16)                      | 0.163(7)   | 56.6 ± 1.8 | 0.429(5)         | 0.357(4)                       | 0.139(6)   | 43.4 ± 1.2 |
| 182   | 1.098(7)          | 3.110(16)                      | 0.165(8)   | 49.7 ± 2.0 | 0.432(5)         | 0.356(4)                       | 0.139(6)   | 50.3 ± 1.3 |
| 180   | 1.097(8)          | 3.106(17)                      | 0.177(10)  | 44.2 ± 1.0 | 0.436(4)         | 0.354(3)                       | 0.131(5)   | 55.8 ± 1.1 |
| 170   | 1.109(11)         | 3.111(18)                      | 0.194(15)  | 28.6 ± 1.8 | 0.439(3)         | 0.354(3)                       | 0.135(3)   | 71.4 ± 1.0 |
| 140   | 1.141(16)         | 3.056(22)                      | 0.245(25)  | 20.4 ± 1.7 | 0.449(3)         | 0.349(2)                       | 0.142(3)   | 79.6 ± 0.9 |
| 100   | 1.165(13)         | 3.102(20)                      | 0.251(20)  | 18.0 ± 1.5 | 0.456(2)         | 0.351(2)                       | 0.154(2)   | 82.0 ± 0.7 |
| 80    | 1.186(14)         | 3.143(20)                      | 0.245(22)  | 16.0 ± 1.4 | 0.463(2)         | 0.355(2)                       | 0.144(2)   | 84.0 ± 0.8 |
| 50    | 1.152(21)         | 3.243(26)                      | 0.209(33)  | 11.6 ± 1.5 | 0.467(2)         | 0.359(2)                       | 0.147(2)   | 88.4 ± 0.9 |
| 30    | 1.167(27)         | 3.206(31)                      | 0.253(44)  | 12.8 ± 1.9 | 0.467(3)         | 0.361(2)                       | 0.153(3)   | 87.2 ± 1.0 |
| 10    | 1.145(20)         | 3.237(25)                      | 0.230(31)  | 12.3 ± 1.4 | 0.467(2)         | 0.358(2)                       | 0.147(2)   | 87.7 ± 0.7 |
| 4.2   | 1.172(13)         | 3.233(20)                      | 0.214(20)  | 12.2 ± 0.9 | 0.468(2)         | 0.360(2)                       | 0.141(1)   | 87.8 ± 0.6 |

\* Estimated standard deviations are given in parentheses.

TABLE 2

Isomer shift ( $\delta$ ) (relative to iron foil), quadrupole splitting ( $\Delta$ ), line width ( $\Gamma/2$ ), and area fraction ( $A$ ) of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , sample B, as a function of temperature <sup>a</sup>

| $T/K$ | High-spin doublet |                                |            | $A(\%)$    | Low-spin doublet |                                |                    | $A(\%)$    |
|-------|-------------------|--------------------------------|------------|------------|------------------|--------------------------------|--------------------|------------|
|       | $\delta$          | $\Delta$<br>mm s <sup>-1</sup> | $\Gamma/2$ |            | $\delta$         | $\Delta$<br>mm s <sup>-1</sup> | $\Gamma/2$         |            |
| 300   | 0.939(5)          | 2.643(13)                      | 0.128(4)   | 100.0      |                  |                                |                    | 0.0        |
| 260   | 1.002(5)          | 2.777(14)                      | 0.122(2)   | 97.5 ± 1.3 | 0.438(50)        | 0.32 <sup>b</sup>              | 0.114 <sup>b</sup> | 2.4 ± 0.6  |
| 220   | 1.023(5)          | 2.880(14)                      | 0.119(2)   | 96.2 ± 1.4 | 0.35(3)          | 0.33 <sup>b</sup>              | 0.113 <sup>b</sup> | 3.7 ± 0.7  |
| 190   | 1.039(5)          | 2.930(15)                      | 0.121(2)   | 93.6 ± 1.3 | 0.436(21)        | 0.331(18)                      | 0.116(27)          | 6.4 ± 0.9  |
| 188   | 1.042(5)          | 2.942(15)                      | 0.119(2)   | 92.2 ± 0.9 | 0.439(17)        | 0.325(13)                      | 0.143(23)          | 7.8 ± 0.7  |
| 186   | 1.039(5)          | 2.935(15)                      | 0.119(15)  | 48.1 ± 1.0 | 0.426(2)         | 0.331(2)                       | 0.118(3)           | 51.9 ± 1.0 |
| 184   | 1.033(6)          | 2.931(15)                      | 0.120(6)   | 22.2 ± 0.9 | 0.425(2)         | 0.329(2)                       | 0.118(2)           | 77.7 ± 0.7 |
| 182   | 1.040(9)          | 2.946(17)                      | 0.118(12)  | 10.0 ± 0.8 | 0.427(2)         | 0.331(2)                       | 0.115(1)           | 89.9 ± 0.6 |
| 180   | 1.027(26)         | 2.918(29)                      | 0.126(39)  | 3.7 ± 0.9  | 0.433(2)         | 0.329(2)                       | 0.115(1)           | 96.2 ± 0.7 |
| 160   | 0.996(52)         | 3.089(55)                      | 0.110(80)  | 1.6 ± 0.9  | 0.434(2)         | 0.334(2)                       | 0.125(2)           | 98.3 ± 0.7 |
| 120   |                   |                                |            | 0.0        | 0.425(2)         | 0.331(2)                       | 0.119(2)           | 100.0      |
| 4.2   |                   |                                |            | 0.0        | 0.461(2)         | 0.335(2)                       | 0.126(2)           | 100.0      |

<sup>a</sup> Estimated standard deviations are given in parentheses. <sup>b</sup> Values held constant in the fitting procedure.

relative accuracy in the temperature measurement was 0.1 K with an absolute accuracy of *ca.* ±3.0 K. The peak profiles were recorded in a step scanning mode and the pulses were stored in a multichannel analyzer (Elscont, MEDA) operating in the multiscanning mode. Details of the apparatus and the sample preparation are given elsewhere.<sup>15</sup>

Two independent differential thermal analysis (d.t.a.) measurements in the temperature region 180–300 K were carried out on both samples. The results from the two laboratories were practically the same.

## RESULTS AND DISCUSSION

**Mössbauer Studies.**—Mössbauer spectra were recorded at various temperatures for samples A and B, with particular emphasis on the transition region. The spectra show clearly the co-existence of the two spin isomers, the high-spin and the low-spin species of iron(II), with strongly temperature-dependent intensities as observed previously.<sup>3</sup> The data of the carefully analyzed spectra are listed in Tables 1 and 2.

Mössbauer spectra of samples A and B (Figure 1 and Tables 1 and 2) show that A contains 12% of the high-

spin species at 4.2 K whereas B contains none. The 'residual' paramagnetism in sample A has been detected previously by magnetic measurements only.

Figure 2 shows the temperature dependence of the quadrupole splitting  $\Delta$ , the line width  $\Gamma/2$ , and the fraction  $x_{\text{HS}} \approx A_{\text{HS}}^*$  of the high-spin state from the Mössbauer spectra and the temperature dependence of the magnetic moment for sample A. A marked change in the Mössbauer line width and a pronounced irregularity in the quadrupole splitting of the high-spin molecules occurs in the critical temperature region,  $T_c$ . Such changes are here reported for the first time in a spin cross-over system. In sample B this could not be observed, because the spin transition is extremely sharp and, hence, practically no high-spin species is present below the transition temperature (see Figure 3).

Our measurements on sample B contradict an earlier

\* The actual fractions of the high-spin and low-spin species may be considered as being approximately equal to the corresponding resonance area fractions, provided the Debye-Waller factors of the two spin isomers do not differ greatly.

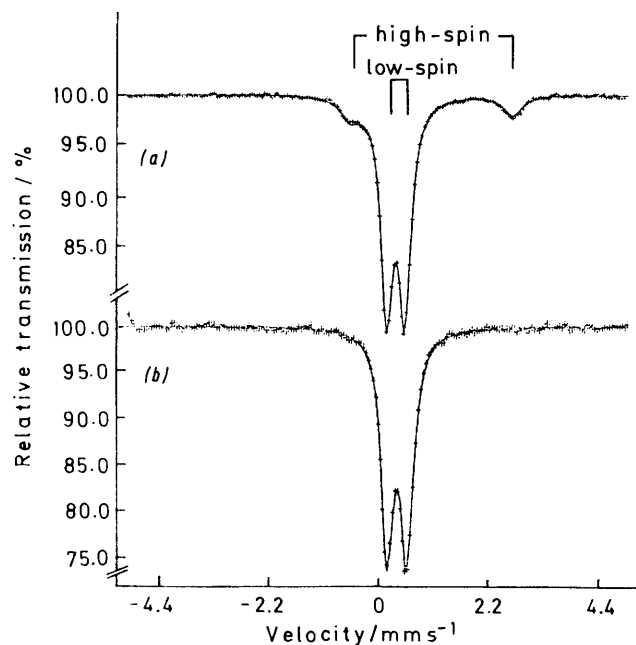


FIGURE 1 Mössbauer absorption spectra [source:  $^{57}\text{Co}$  in Rh at 293 K] of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  at 4.2 K: (a) sample A; (b) sample B

report<sup>16</sup> that a well formed crystalline product from acetone extraction showed no cross-over and maintained high-spin characteristics down to the temperature of liquid nitrogen, whereas on storage of this substance over water, it eventually showed the normal cross-over.

The spin transition in sample B is much sharper than in sample A, as seen from Figure 4, which shows the

temperature dependence of the high-spin fraction  $x_{\text{HS}}$  evaluated from the Mössbauer spectra of the two samples.

The unusual temperature dependence of the quadrupole splitting of the high-spin state in sample A near  $T_c$  suggests that a reorganisation of the lattice sites accompanies the spin cross-over. The line widths of the high-spin iron(II) molecules at low temperatures are almost twice those at higher temperatures. With the assumption of two lattice sites for the high-spin iron(II) species a meaningful fit of the recorded spectra was not possible. The abrupt change in the line width of the high-spin resonance near  $T_c$  may be indicative of one type of lattice changing into another along with the spin cross-over.

*Differential Thermal Analysis and Magnetic Susceptibility Studies.*—The different transition characteristics also manifest themselves in a d.t.a. plot (see Figure 5). Based on precise heat capacity measurements, it has previously been suggested<sup>9</sup> that the phase transformation in  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  is of first order. Existence of a measurable latent heat and hysteresis are generally taken as characteristics of a first-order transformation. However, careful magnetic susceptibility (see Figure 6) and Mössbauer measurements on sample B could not reveal any hysteresis of a width  $>0.2$  K.

In many first-order phase transitions as in the case of alkali-metal sulphates,<sup>17</sup> there is superposition of second-order behaviour. A large number of order-disorder changes start as  $\lambda$  transitions and are seen as abrupt (first-order) changes towards completion.<sup>17</sup> In view of the remarkable differences in the d.t.a. (see Figure 5) measurements on samples A and B and in the light of the above discussion, it is quite likely that the

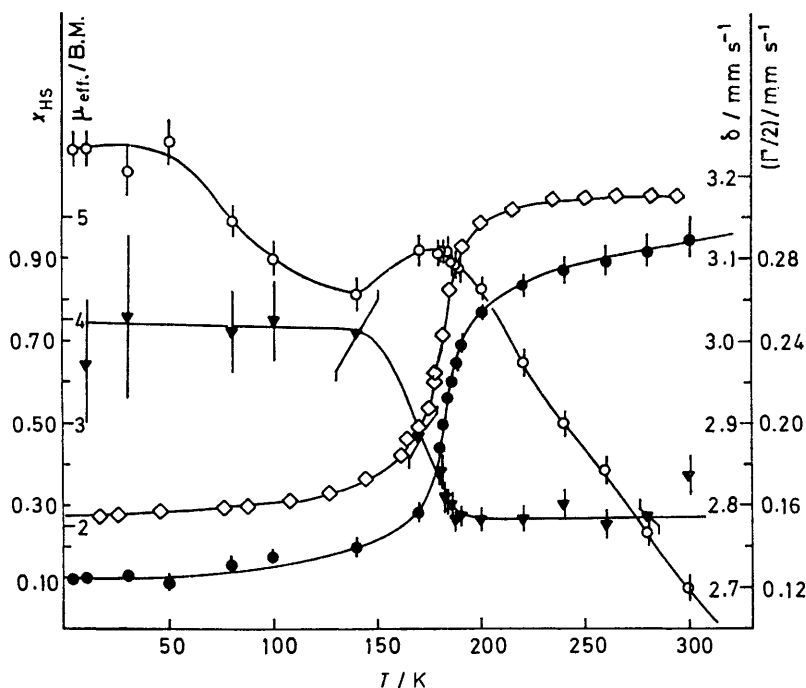


FIGURE 2 Quadrupole splitting (○), line width (▼), area fraction (●), and effective magnetic moment (◇) of the high-spin state in  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , sample A, as a function of temperature (1 B.M. =  $9.274 \times 10^{-24}$  A m<sup>2</sup>)

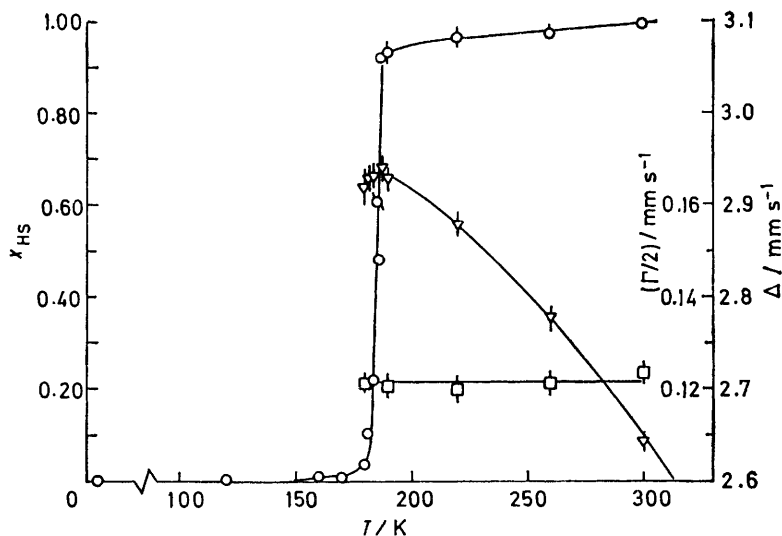


FIGURE 3 Quadrupole splitting ( $\nabla$ ), line width ( $\square$ ), and area fraction ( $\circ$ ) of the high-spin state in  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , sample B, as a function of temperature

phase transition in  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  has a mixed character. Therefore, the failure to detect hysteresis is not too surprising.

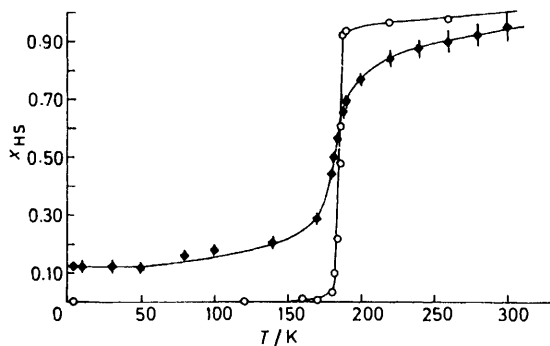


FIGURE 4 High-spin fraction  $x_{\text{HS}}$  from the Mössbauer spectra of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  as a function of temperature: sample A ( $\circ$ ) and sample B ( $\blacklozenge$ )

A time dependence of the magnetic susceptibility at  $T_c$  observed in earlier studies<sup>4</sup> has also been confirmed by us.

**X-Ray Diffractometry.**—In order to confirm the above suggestion, X-ray diffractometric measurements between 80 and 300 K were carried out on samples A and B. The Bragg angles  $2\theta$  from 0 to  $50^\circ$  were scanned as a function of temperature. A large number of reflections were obtained; a few representative spectra of scans between  $19$  and  $26^\circ$  for the two samples, where essential changes appear, are shown in Figures 7 and 8. In both samples A and B, two new peaks appear on cooling, one around  $20.5^\circ$ , and another one as a shoulder on the very intense  $24^\circ$  peak. Simultaneously, one of the group of three peaks in the range  $22$ – $24^\circ$  disappears below  $T_c$ . The peaks also shift to higher angles with decreasing temperatures. Other differences in the X-ray spectral features between A and B are the following. The line widths of the signals from sample A are broader than

those of sample B. This is most probably due to the fact that sample A consists of much smaller crystallites than sample B. The peaks at lower temperatures for sample A are *considerably* broader than those of sample B, which remain distinctly sharp, except for the abrupt disappearance of the peak around  $23^\circ$ . This pronounced

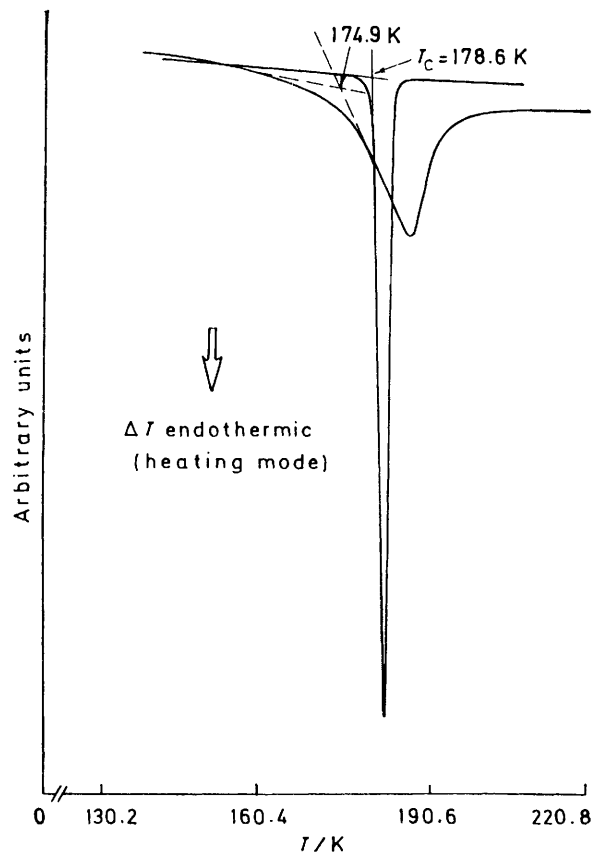


FIGURE 5 D.t.a. curves for samples A and B of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$

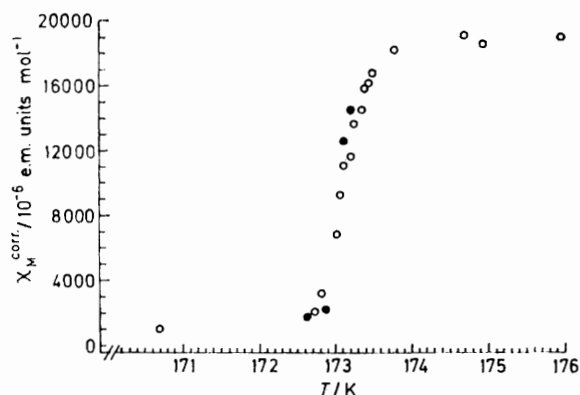


FIGURE 6 Magnetic susceptibility data in the transition region of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , sample B, recorded in cooling mode ( $\circ$ ) and heating mode ( $\bullet$ ). (Note the small temperature intervals)

broadening effect in sample A below  $T_c$  confirms that even at these temperatures a noticeable amount of the high-temperature phase persists. These observations are in agreement with the Mössbauer and magnetic susceptibility results on sample A. In the case of sample B, however, as shown in Figure 4, the transition is very abrupt and complete, and only the low-temperature phase is present below  $T_c$ . Previous X-ray investigations (Debye-Scherrer powder photographs) at room tem-

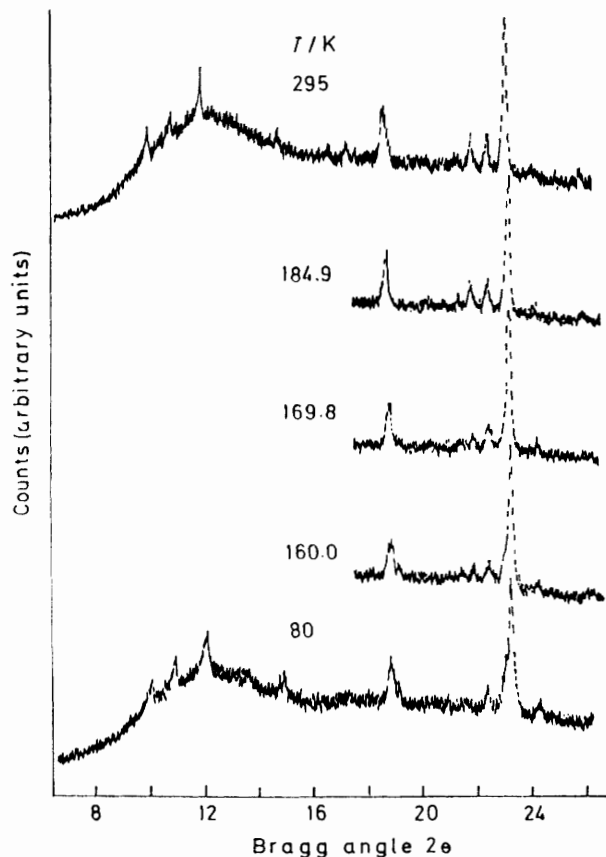


FIGURE 7 Peak profiles of X-ray powder diffraction of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , sample A, as a function of temperature

perature and below failed to detect any structural phase change in  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ .<sup>2,5</sup>

The fact that the overall features of the X-ray diffractometric spectra of the high- and low-temperature phases are not too different implies that the structural characteristics of the two phases are quite similar. Nevertheless, in view of the marked changes in the

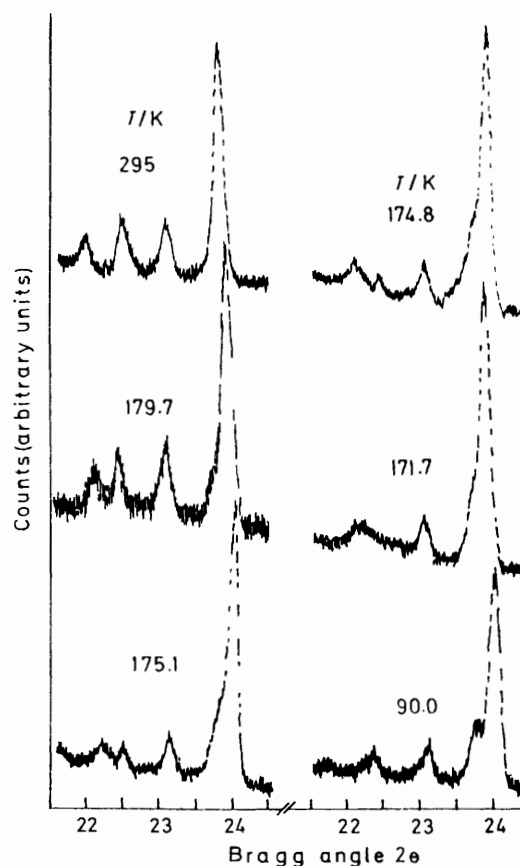


FIGURE 8 Peak profiles of X-ray powder diffraction of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , sample B, as a function of temperature

Mössbauer resonance line width and the quadrupole splitting of the high-spin phase near  $T_c$ , as well as the differences in the X-ray diffractometric pattern between the high- and low-temperature phases, some kind of structural reorganization, other than the well known change in iron-ligand bond length induced by the spin transition, can no longer be excluded.

From temperature-dependent X-ray measurements on single crystals of  $[\text{Fe}(\text{amp})_3]\text{Cl}_2 \cdot \text{EtOH}$  (amp = 2-amino-methylpyridine),<sup>18</sup> which also shows a temperature-dependent high-spin  $\rightleftharpoons$  low-spin transition, it has been found that the ethanol molecules undergo an orientational order-disorder transition, which is suggested as initiating the spin transition. It is quite likely that in  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  too, a structural order-disorder transition of an orientational kind triggers the high-spin  $\rightleftharpoons$  low-spin cross-over. It is possible that the co-ordinated NCS groups occupy different rotational positions on heating. This process, when accompanied by an

increase in the metal–ligand bond length, may well be such as to induce the spin change. It would also explain the irregularities in the temperature dependence of the quadrupole splitting line width of the high-spin phase near  $T_c$ . Temperature-dependent X-ray structural analyses on single crystals are badly needed to clarify this point.

As observed in other cases,<sup>19</sup> the present studies once more demonstrate that the spin cross-over characteristics may be highly susceptible to the method of preparation. Our samples A and B differ in size and quality of the crystals. Method A not only yields a more finely dispersed material than the extraction method, B, but the rapid precipitation method will also incorporate more imperfections into the crystallites than method B which leads to bigger and more perfect crystallites. A more detailed study of the effect of crystal defects on the spin-transition characteristics is presently underway.

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## REFERENCES

- <sup>1</sup> W. A. Baker, jun., and H. M. Bobonich, *Inorg. Chem.*, 1964, **3**, 1184.
- <sup>2</sup> E. König and K. Madeja, *Inorg. Chem.*, 1967, **6**, 48.
- <sup>3</sup> I. Dézsi, B. Molnár, T. Tarnoczi, and K. Tompa, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2486.
- <sup>4</sup> A. T. Casey and F. Isaac, *Austral. J. Chem.*, 1967, **20**, 2765.
- <sup>5</sup> W. A. Baker, jun., and G. J. Long, *Chem. Comm.*, 1965, 368.
- <sup>6</sup> E. König and K. Madeja, *Spectrochim. Acta*, 1967, **A23**, 45.
- <sup>7</sup> J. H. Takemoto and B. Hutchinson, *Inorg. Chem.*, 1973, **12**, 705.
- <sup>8</sup> J. R. Ferraro and J. Takemoto, *Appl. Spectroscopy*, 1974, **28**, 66.
- <sup>9</sup> M. Sorai and S. Seki, *J. Phys. and Chem. Solids*, 1974, **35**, 555.
- <sup>10</sup> M. Sorai and S. Seki, *J. Phys. Soc. Japan*, 1972, **33**, 575.
- <sup>11</sup> P. Ganguli and P. Gütllich, *J. Physique*, 1980, **41**, C1–313.
- <sup>12</sup> J. Ensling, Ph.D. Thesis, TH Darmstadt, West Germany, 1970.
- <sup>13</sup> K. Madeja, W. Wilke, and S. Schmidt, *Z. anorg. Chem.*, 1966, **346**, 306.
- <sup>14</sup> E. Kankleit in 'Mössbauer Effect Methodology,' ed. I. J. Gruverman, Plenum Press, New York, 1965, vol. 1.
- <sup>15</sup> W. Irlner, Ph.D. Thesis, Universität Erlangen-Nürnberg, West Germany, 1979.
- <sup>16</sup> A. G. Maddock and J. J. Schleiffer, *J.C.S. Dalton*, 1977, 617.
- <sup>17</sup> C. N. R. Rao and K. J. Rao, 'Phase Transition in Solids,' McGraw-Hill, New York, 1978.
- <sup>18</sup> M. Mikami, M. Konno, and Y. Saito, *Chem. Phys. Letters*, 1979, **63**, 566.
- <sup>19</sup> E. König, K. Madeja, and K. J. Watson, *J. Amer. Chem. Soc.*, 1968, **90**, 1146.