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Nature of the Continuous High-Spin ($^5\mathrm{T}_2$) $\rightleftharpoons$ Low-Spin ($^1\mathrm{A}_1$) Transition in Solid (Dithiocyanato)bis(2,2′-bi(5-methyl-2-thiazoline))iron(II). Anomalous Behavior of Total Effective Thickness, Quadrupole Splitting, Line Widths, and Lattice Spacings Employing Mössbauer Effect and X-ray Diffraction

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Abstract: The gradual high-spin ($S = 2$; $^5\mathrm{T}_2$) $\rightleftharpoons$ low-spin ($S = 0$; $^1\mathrm{A}_1$) transformation in solid $[\mathrm{Fe(bts)_2(NCS)_2}]$ (bts = 2,2′-bi(5-methyl-2-thiazoline)) has been studied by variable-temperature ^{57}Fe Mössbauer effect and X-ray diffraction. The ground states involved are characterized, at the transition temperature $T_c \approx 219.5$ K, by the quadrupole splitting $\Delta E_Q(^5\mathrm{T}_2) = 2.84$ mm s^{-1}, $\Delta E_Q(^1\mathrm{A}_1) = 0.59$ mm s^{-1} and the isomer shift $\delta^{\mathrm{IS}}(^5\mathrm{T}_2) = 1.01$ mm s^{-1}, $\delta^{\mathrm{IS}}(^1\mathrm{A}_1) = 0.35$ mm s^{-1}. The temperature dependence of $-\ln(\sum t_i)$, where t_i is the effective thickness ($i = {}^5\mathrm{T}_2, {}^1\mathrm{A}_1$), shows a nonlinear behavior consistent with different Debye–Waller factors, $-\ln f_{^5\mathrm{T}_2}$ and $-\ln f_{^1\mathrm{A}_1}$. The same conclusion derives from the observation of different temperature factors for the isomer shift. The temperature function of $\Delta E_Q(^5\mathrm{T}_2)$ depends on whether the $^5\mathrm{T}_2$ isomer is incorporated into the minority or the majority constituent. The absorber line width for the minority constituent Γ_i^{abs} is excessive and tends to normal values as the spin transition proceeds, a result attributed to the distribution of ΔE_Q values. The lattice spacings derived from X-ray diffraction show a continuous shift with temperature that parallels that of the $^5\mathrm{T}_2$ fraction, $n_{^5\mathrm{T}_2}$. The observations are interpreted by formation of a solid solution of the two spin isomers within the same lattice. As a consequence, the continuous character of the transition is consistent with the assumption of weak cooperative interaction between the individual complexes and a wide distribution of the nuclei of the minority constituent.

It is well-known that transitions of the type high-spin ($^5\mathrm{T}_2$) $\rightleftharpoons$ low-spin ($^1\mathrm{A}_1$) may exhibit either an essentially discontinuous or a more gradual behavior.[3-5] The almost discontinuous transitions in $[\mathrm{Fe(phen)_2(NCS)_2}]$ and $[\mathrm{Fe(phen)_2(NCSe)_2}]$ (where phen = 1,10-phenanthroline) have been shown, on the basis of heat capacity measurements, to be thermodynamically of first order.[6] Moreover, the observation of hysteresis has been employed as an indication of the first-order character of the abrupt spin transitions. Thus, hysteresis effects have been reported for $[\mathrm{Fe(4,7\text{-}(CH_3)_2phen)_2(NCS)_2}]$,[7,8] $[\mathrm{Fe(bi)_3}](\mathrm{ClO_4})_2$ (where bi = 2,2′-bi-2-imidazoline),[9] and several additional iron(II) complexes.[10-13]

The detailed characterization of the high-spin ($^5\mathrm{T}_2$) $\rightleftharpoons$ low-spin ($^1\mathrm{A}_1$) transitions of the gradual type proved to be considerably more difficult. First of all, the classification into the two types of transition is by no means trivial. There are transitions such as that in $[\mathrm{Fe(paptH)_2}](\mathrm{NO_3})_2$ (where paptH = 2-(2-pyridylamino)-4-(2-pyridyl)thiazole),[10] which appear to be continuous, although the observation of a pronounced hysteresis shows them to be of first order. Secondly, transformations between transitions of discontinuous and apparently gradual type have been reported; such as that in $[\mathrm{Fe(phy)_2}](\mathrm{ClO_4})_2$ (where phy = 1,10-phenanthroline-2-carbaldehyde phenylhydrazone) which is effected by a simple recrystallization.[11] Most of the physical methods employed have not been very helpful for the understanding of the spin transitions of continuous type. In particular, some attempts at the determination of individual Debye–Waller factors for the two ground states, high-spin $^5\mathrm{T}_2$ and low-spin $^1\mathrm{A}_1$, have been made,[14] although the results have not been conclusive.

Recently, various theoretical models have been conceived in order to provide an interpretation of the high-spin $\rightleftharpoons$ low-spin transitions. In the present context, reference is given only to a few.[15-20] These studies seem to account rather well for the general observation that both abrupt and gradual type of transition are often found even for closely related compounds. In any particular model, the type of transition is determined by the specific numerical values which are adopted for certain parameters. Thus, in an Ising-type model,[15] an interaction term is introduced such that the energy of the $^5\mathrm{T}_2$ and $^1\mathrm{A}_1$ states of a given ion depends on the spin state of neighboring ions. The characteristic parameter is J/kT_c where J is the interaction constant for the $^5\mathrm{T}_2$ ions and T_c the transition temperature. A gradual transition then results for $J/kT_c < 2.0$, whereas abrupt transitions are obtained if $J/kT_c \geq 2.0$ (orbital splitting parameters $\Delta_1 = \Delta_2 = 500$ cm^{-1}, spin–orbit coupling constant $\lambda = -100$ cm^{-1}, and $T_c = 150$ K assumed[15]). In a cluster or domain model,[6,16] it is proposed that the trans-

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formation takes place within domains in which all iron atoms have the same spin. The characteristic parameter is the number of molecules (n) per cluster, i.e., the domain size. For abrupt transitions, e.g., in $[Fe(phen)_2(NCS)_2]$ and $[Fe(phen)_2(NCSe)_2]$, the values of $n = 95$ and $n = 77$, respectively, have been obtained,[6] whereas for the gradual transition in $[Fe(2\text{-pic})_3]Cl_2 \cdot C_2H_5OH$ (where 2-pic = 2-(aminomethyl)pyridine), $n \approx 3.5$ has been estimated.[16] It should be noted that recent measurements of the relaxation time T_1 for protons in $[Fe(phen)_2(NCS)_2]$ are in conflict with the cluster model, whereas excellent agreement with the Ising-type model has been found.[17]

The interest in spin transition systems has been plagued from the start by the sensitivity of the physical properties, in the transition region, toward compound preparation and even toward the difficult controllable subtle variations in the preparation by the same method. More recently, the study of grinding and doping effects in the compound $[Fe(3\text{-}OCH_3SalEen)_2]PF_6$ (where 3-OCH_3SalEen = monoanion of *N*((ethylamino)ethyl)-3-methoxysalicylideneamine)[21,22] as well as related investigations on $[Fe_xZn_{1-x}(2\text{-pic})_3]Cl_2 \cdot C_2H_5OH$[13] and $[Fe(4,7\text{-}(CH_3)_2phen)_2(NCS)_2] \cdot \alpha$-picoline[23] have demonstrated that grain size and lattice defects introduced by these processes, such as crystal dislocations, vacancies, and impurities, are of importance. In particular, the character of the transition, i.e., whether abrupt or more gradual, seems to be determined by properties of the solid rather than by intra or intermolecular parameters, at least for the compounds subject to these studies.

The question then arises about the nature of those spin transitions which are of the continuous type and do not show any hysteresis effects or any other evidence for a first-order phase change. In order to successfully study this problem, certain conditions have to be met by the sample. These include completeness of the transition at both high and low temperatures, nonoverlapping Mössbauer absorption lines for the two spin isomers, $^5T_2$ and $^1A_1$, reproducibility toward the sample preparation, absence of impurities, etc. The recently reported[24] spin transition complex $[Fe(bts)_2(NCS)_2]$ (where bts = 2,2′-bi(5-methyl-2-thiazoline)) seems to be a suitable candidate for such an investigation. The effective magnetic moment of the compound of ca. 5.26 μ_B at 293 K decreases gradually to assume a value of 0.84 μ_B at 93 K. On the basis of the temperature dependence of μ_{eff} and preliminary ^{57}Fe Mössbauer spectra,[24] the transition is expected to be practically complete both at 293 and 93 K. In the present contribution we report, therefore, the results of a detailed and accurate analysis of the high-spin ($^5T_2$) ⇌ low-spin ($^1A_1$) transition in this compound based on ^{57}Fe Mössbauer effect and X-ray powder diffraction measurements.

Experimental Section

Materials. 2,2′-Bi(5-methyl-2-thiazoline) as well as the samples of (diisothiocyanato)bis(2,2′-bi(5-methyl-2-thiazoline))iron(II), $[Fe(bts)_2(NCS)_2]$, have been prepared as described elsewhere.[24] All samples gave satisfactory analyses, their physical data being in agreement with those previously reported.[24]

Methods. ^{57}Fe Mössbauer spectra were measured as described in detail in our previous reports.[9,11] All velocity scales and isomer shifts are referred to a metallic iron standard at 298 K. To convert to the sodium nitroprusside scale, add +0.257 mm s^{-1}. The quantities derived from a computer-based decomposition of the areas into Lorentzians are defined as follows. The effective thickness t_i of an individual peak is derived from its background corrected area, A_i, using the relation

$$A_i = 0.5\pi\Gamma f_S \frac{t_i}{1 + 0.25t_i} \qquad (1)$$

Here, $0.5\pi\Gamma f_S$ is a scaling factor which is determined from the spectra of standard materials, the individual quantities having been defined

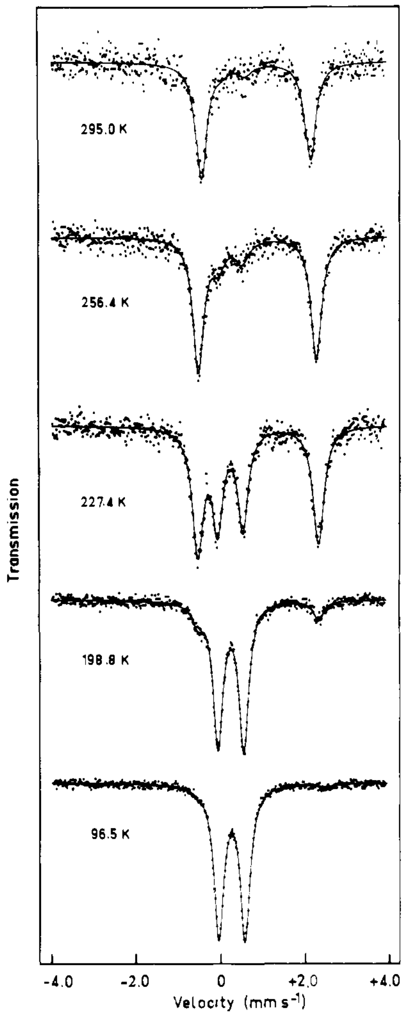

Figure 1. ^{57}Fe Mössbauer effect spectra of $[Fe(bts)_2(NCS)_2]$ at 96.5, 198.8, 227.4, 256.4, and 295.0 K. The transition is centered at $T_c \approx$ 219.5 K.

elsewhere.[9,11] The effective thickness for the two phases $t_{^5T_2}$ and $t_{^1A_1}$ which are sums of their individual component values t_i are also given by

$$t_{^5T_2} = dn_{^5T_2}f_{^5T_2} \qquad (2)$$

$$t_{^1A_1} = d(1 - n_{^5T_2})f_{^1A_1}$$

In eq 2, $n_{^5T_2}$ is the high-spin fraction, $f_{^5T_2}$ and $f_{^1A_1}$ are the recoil-free fractions for the two phases, and $d = N\beta\delta\sigma_0$, the quantities involved having the usual meaning.[11]

The absorber line widths for the two phases, $\Gamma_{^5T_2}{}^{abs}$ and $\Gamma_{^1A_1}{}^{abs}$, may be obtained from the observed line widths, $\Gamma_{obsd}{}^{^5T_2}$ and $\Gamma_{obsd}{}^{^1A_1}$, if corrections for the finite thickness effect are introduced. Thus, to a good approximation, it is

$$\Gamma_{obsd}{}^{^5T_2} = \Gamma_S + \Gamma_{^5T_2}{}^{abs} + 0.27\Gamma_S{}^{\circ}0.5t_{^5T_2} + \Gamma_{instr} \qquad (3)$$

$$\Gamma_{obsd}{}^{^1A_1} = \Gamma_S + \Gamma_{^1A_1}{}^{abs} + 0.27\Gamma_S{}^{\circ}0.5t_{^1A_1} + \Gamma_{instr}$$

Here, Γ_S is the line width of the source, $\Gamma_S{}^{\circ} = 0.097$ mm s^{-1} is the natural line width of the source, and Γ_{instr} the broadening due to instrumental factors. The latter correction can be taken to be equal for both the phases as these are always recorded simultaneously. The factor of one-half of the third term of eq 3 arises since the expressions apply otherwise to a single peak of either phase. The small texture effects have been neglected. Measurements of X-ray powder diffraction have been performed in the mode of step scanning of the diffractometer, the steps being 0.005° in 2θ. More details have been given elsewhere.[11,25]

Results

^{57}Fe Mössbauer Effect. Temperature Dependence of Quadrupole Splitting and Isomer Shift. Two independently prepared samples of $[Fe(bts)_2(NCS)_2]$ have been studied between 96.5 and 295.0

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Table I. ^{57}Fe Mössbauer Effect Parameters of $[Fe(bts)_2(NCS)_2]$ for a Set of Representative Temperatures[a]

T, K	ΔE_Q-($^1A_1$),[b] mm s^{-1}	δ^{IS}-($^1A_1$),[c] mm s^{-1}	ΔE_Q-($^5T_2$),[b] mm s^{-1}	δ^{IS}-($^5T_2$),[c] mm s^{-1}	$t_{^5T_2}/t_{total}$
96.5	0.62	0.37	3.03 ± 0.08	1.06 ± 0.05	0.03
131.6	0.62	0.37	2.96 ± 0.08	1.08 ± 0.04	0.04
188.9	0.61	0.35	2.86 ± 0.06	1.04 ± 0.04	0.08
198.8	0.61	0.35	2.86	1.01	0.119
206.5	0.60	0.35	2.85	1.01	0.197
212.0	0.61	0.34	2.86	1.01	0.268
220.0	0.59	0.35	2.84	1.01	0.412
227.4	0.60	0.35	2.85	1.01	0.574
235.2	0.59	0.34	2.84	1.00	0.677
238.7	0.58	0.35	2.83	1.00	0.698
247.7	0.56	0.33	2.84	1.00	0.740
256.4	0.56	0.35	2.79	0.95	0.770
264.4	0.54 ± 0.02	0.36	2.78	0.99	0.780
272.7			2.77	0.98	0.798
281.5			2.75	0.98	0.784
291.5			2.72	0.98	0.826

[a] The data in the temperature interval between 96.5 and 188.9 K are practically unchanged and are therefore not listed in detail. The presented data are for increasing temperatures. For decreasing temperatures, almost identical data have been obtained. [b] Experimental uncertainty ±0.01 mm s^{-1} except where stated. [c] Isomer shifts δ^{IS} are listed relative to natural iron at 298 K. Experimental uncertainty ±0.01 mm s^{-1} except where stated.

K. For one of the samples, Figure 1 shows five typical spectra, i.e., those collected at 96.5, 198.8, 227.4, 256.4, and 295.0 K. The distinct spectrum at 96.5 K is characterized by the quadrupole splitting $\Delta E_Q = 0.62 \pm 0.01$ mm s^{-1} and the isomer shift $\delta^{IS} = 0.37 \pm 0.01$ mm s^{-1}, the value of δ^{IS} being typical for a low-spin $^1A_1$ ground state of iron(II). At 198.8 K, a second weak doublet may clearly be recognized, its intensity increasing with increasing temperature, while that of the first doublet is simultaneously decreasing; cf. spectrum at 227.4 K. At 256.4 K, the contribution of the second doublet is clearly predominant, and at 295.0 K, it is almost the only one present. On the basis of the Mössbauer parameters, i.e., $\Delta E_Q = 2.72 \pm 0.01$ mm s^{-1}, $\delta^{IS} = 0.98 \pm 0.01$ mm s^{-1} at 291.5 K, the second doublet may be assigned to the high-spin $^5T_2$ ground state of iron(II). It is thus evident that a high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition is involved in $[Fe(bts)_2(NCS)_2]$. Although the transition is of the continuous type, the larger part of the transformation is accomplished within a relatively narrow temperature range. The detailed values of the Mössbauer parameters including the relative effective thickness $t_{^5T_2}/t_{total}$ are listed in Table I for a representative set of temperatures. It should be noted that the values of $t_{^5T_2}/t_{total}$ qualitatively represent the behavior of the high-spin fraction but for the difference in recoil-free fraction of the two phases. This is illustrated by Figure 2 where the quantities $t_{^5T_2}/t_{total}$ and $n_{^5T_2}$ are plotted simultaneously as a function of temperature. If the temperature is gradually lowered, the $^5T_2$ spectrum changes over into the $^1A_1$ spectrum in much the same proportion as observed for the transformation $^1A_1 \rightarrow {}^5T_2$. In particular, practically identical values of $t_{^5T_2}/t_{total}$ are obtained at the same temperature. It follows that no hysteresis is associated with the spin transition in $[Fe(bts)_2(NCS)_2]$. Altogether, spectra at 27 temperatures have been measured. The transition temperature T_c is usually defined as the temperature at which the high-spin fraction $n_{^5T_2} = 0.50$. From the results derived in the next section, it is found that $T_c \approx 219.5$ K.

There is a pronounced temperature dependence of the quadrupole splitting for the $^5T_2$ state $\Delta E_Q(^5T_2)$ which is illustrated in Figure 3. It may be easily recognized that the temperature function of $\Delta E_Q(^5T_2)$ for the residual high-spin molecules is showing a significant discontinuity in the region slightly below T_c.

A careful inspection of the isomeric shifts δ^{IS} for the two constituents, in those temperature regions where the applicable errors in their estimation are small, suggests that their temperature dependence is significantly different. A linear fit of the data for the low-spin $^1A_1$ isomer between 96.5 and 235 K gives $\partial(\delta^{IS})/\partial T = -(2.4 \pm 0.1) \times 10^{-4}$ mm s^{-1} K^{-1}, whereas the corresponding value for the high-spin $^5T_2$ isomer between 205 and 300 K is obtained as $-(5.1 \pm 0.3) \times 10^{-4}$ mm s^{-1} K^{-1}. This temperature dependence arises from the second-order Doppler effect.

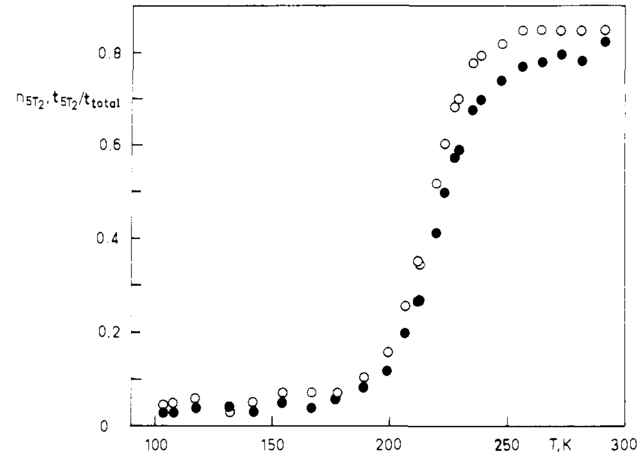

Figure 2. Temperature dependence of the effective thickness for the high-spin $^5T_2$ constituent, $t_{^5T_2}/t_{total}$, for both increasing and decreasing temperatures (●) and the derived values of the $^5T_2$ fraction, $n_{^5T_2}$ (○).

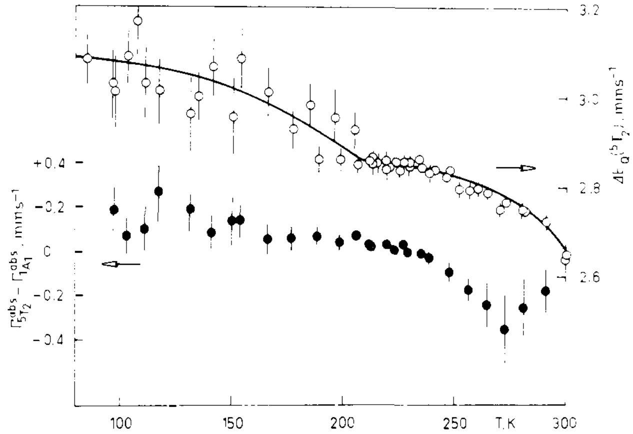

Figure 3. Temperature dependence of the quadrupole splitting for the high-spin $^5T_2$ ground state, $\Delta E_Q(^5T_2)$ (data collected for two different sets of observations); and temperature dependence of the difference in absorber line widths $\Delta\Gamma^{abs} = (\Gamma_{^5T_2}{}^{abs} - \Gamma_{^1A_1}{}^{abs})$ for $[Fe(bts)_2(NCS)_2]$. Error bars are marked only where larger than the size of the notation.

The second sample of $[Fe(bts)_2(NCS)_2]$ produced results practically identical to those of the first sample.

Quantities Derived from Mössbauer Effect Areas. Temperature Dependence of Total Effective Thickness and Line Widths. Following the procedure outlined in the Experimental Section, the effective thickness t_i, $i = {}^5T_2, {}^1A_1$, has been obtained for the two ground states individually, the quantity $-\ln(\sum t_i)$ being displayed in Figure 4 as a function of temperature. Inspection shows that a clear curvature is formed in the region around T_c. From the slope of the curve, at temperatures sufficiently distant from T_c, i.e., where the lattice consists primarily of one of the two spin isomers, it follows that the recoil-free fraction for the $^1A_1$ constituent, $f_{^1A_1}$, should be higher than that for the $^5T_2$ constituent, $f_{^5T_2}$. Despite this qualitative result, the detailed determination of $f_{^1A_1}$ and $f_{^5T_2}$ for molecular compounds can be performed only under certain simplifying assumptions. Since the applicability of these assumptions to the present problem is questionable, the details of the determination are given in the Appendix.

Another quantity which may be derived from the ^{57}Fe Mössbauer effect areas is the absorber line width. Figure 3 shows the difference of the absorber line widths for the two ground states, $\Delta\Gamma^{abs} = \Gamma_{^5T_2}{}^{abs} - \Gamma_{^1A_1}{}^{abs}$, as a function of temperature. The data

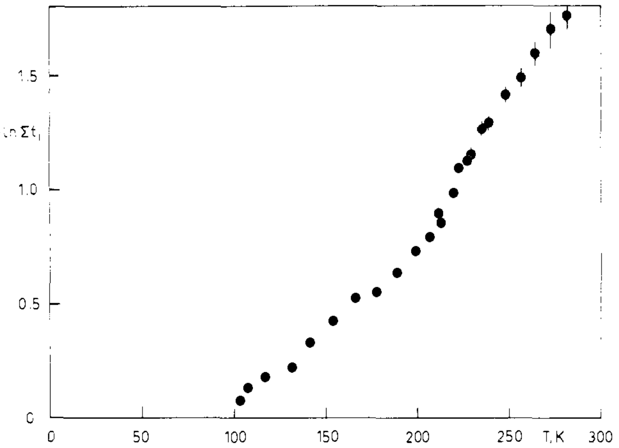

Figure 4. Temperature dependence of the quantity $-\ln(\sum t_i)$, $i = {}^5T_2$, ${}^1A_1$ where t_i is the effective thickness for the respective ground state i, on the basis of ^{57}Fe Mössbauer effect measurements for $[Fe(bts)_2(NCS)_2]$. The vertical error bars are marked only if larger than the size of the notation. They represent the sum of the fitting errors which arise in the estimation of t_i for the individual phases.

have been obtained on the basis of eq 4. Evidently, the quantity $|\Gamma_{^5T_2}{}^{abs} - \Gamma_{^1A_1}{}^{abs}|$ passes through a minimum around T_c or, in an equivalent statement, $\Delta\Gamma^{abs}$ changes its sign. The error bars shown on the $\Gamma_{^5T_2}{}^{abs} - \Gamma_{^1A_1}{}^{abs}$ function in Figure 3 are the sum of the errors for both $^1A_1$ and $^5T_2$ line widths. In the transition region, these errors are rather small. For temperatures higher or lower than T_c, the uncertainty in the estimation of the minority-constituent line width is increasing and thus the errors are increasing correspondingly. The observed variation of $\Delta\Gamma^{abs}$ suggests that the line width for the minority constituent is significantly larger than that for the majority constituent, whereas if the fractional contributions of the two spin isomers are comparable, their line widths are also not significantly different.

X-ray Powder Diffraction. Temperature Dependence of Lattice Spacings. A number of X-ray diffraction patterns have been recorded for $[Fe(bts)_2(NCS)_2]$ at various temperatures and these were found to be rather complex and overlapping. From the comparison of these patterns it is evident that, in contrast to the situation for discontinuous transitions,[8,9,11,12] no new peaks emerge in the spin transition region, although a systematic shift in the peak positions is observed. In order to make a quantitative analysis of the shifts feasible, the temperature dependence of peak profiles has been studied in detail for two intense peaks between 100.0 and 300.0 K. The two peaks were selected since these were well resolved and most likely represent single peaks. The peak profiles have been least-squares fitted to individual Gaussian line shapes in order to obtain accurate values for peak position and line width. Figure 5 illustrates the change with temperature encountered for these two Bragg reflections, i.e., at the diffraction angles θ = 11.118° (line I) and θ = 11.670° (line II) for 115 K. Evidently, line I shifts to 10.955° for $T_c \approx 220$ K and to 10.884° for 300 K. Similarly, line II is found at 11.511° for $T_c \approx 220$ K and at 11.429° for 300 K. Note that the most significant part of the shift which arises around T_c is clearly attributable to the spin transition. From the fit it is also evident that the line width of the reflections remains almost equal over the range of temperatures studied. The full width at half-maximum height, measured in terms of 2θ, is 0.26° ± 0.02° for line I and 0.32° ± 0.02° for line II. This result implies that the two spin isomers, high-spin $^5T_2$ and low-spin $^1A_1$, of $[Fe(bts)_2(NCS)_2]$ are co-existing within the *same* lattice. The obtained results have been also employed to estimate the values of lattice spacings d_{hkl} for the two selected Bragg reflections. Figure 6 shows the variation of the lattice spacings with temperature in comparison with the temperature change of the high-spin fraction $n_{^5T_2}$, as derived from the analysis of the Mössbauer spectra (cf. Appendix). It is easily visualized that the temperature behavior of both types of quantities is closely analogous. The observed change of lattice spacings establishes the volume expansion associated with the spin transition, and moreover, it is consistent with the behavior of the recoil-free fractions for the two isomers. Also notable is the small increase of lattice spacings which shows up in temperature regions more distant from T_c. This effect is due to the thermal expansion of the lattice. Obviously, this variation is absent from the curve for the temperature variation of $n_{^5T_2}$.

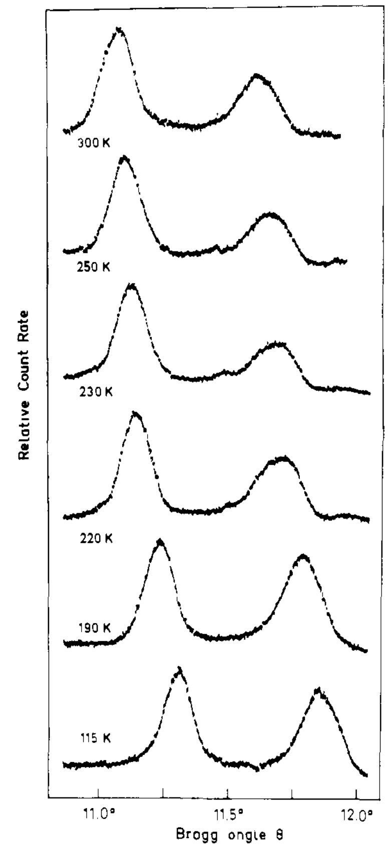

Figure 5. X-ray diffraction peak profiles for two intense Bragg reflections of $[Fe(bts)_2(NCS)_2]$ at θ = 11.307° and θ = 11.860° (for 115 K) at various temperatures.

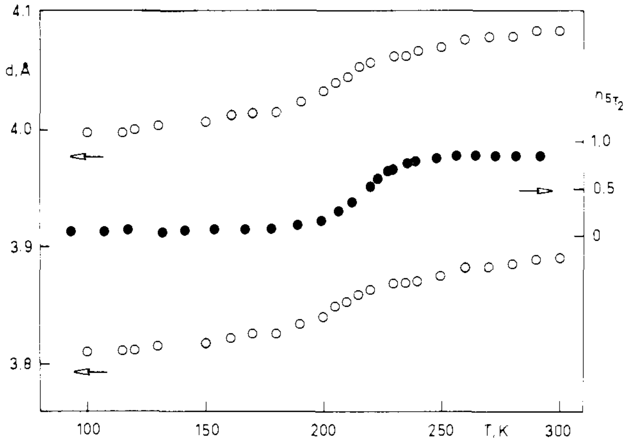

Figure 6. Temperature dependence of the lattice spacings d_{hkl} for the two Bragg reflections of Figure 5 from X-ray diffraction. Comparison with the high-spin fraction $n_{^5T_2}$ from Mössbauer effect measurements.

Discussion

In contrast to a number of spin transitions which have been established as first order,[7-13] the high-spin ($^5T_2$) $\rightleftharpoons$ low-spin ($^1A_1$) transition in $[Fe(bts)_2(NCS)_2]$ may be described in terms of a continuous change with temperature of important physical properties, such as the effective magnetic moment, the $^5T_2$ fraction derived from the ^{57}Fe Mössbauer effect, and the lattice spacings derived from X-ray diffraction. No hysteresis effects have been observed for any of these quantities. The residual fraction of the

$^5T_2$ state at low temperatures is lower than 0.04, and that of the $^1A_1$ state at high temperatures is lower than 0.15, the transition being relatively complete at both temperature ends. Consequently, [Fe(bts)$_2$(NCS)$_2$] may be considered as a representative example of compounds showing a spin transition of the continuous type in the absence of hysteresis.

Of the results derived in the present study, the curvature in the temperature function of $-\ln(\sum t_i)$, in the region of T_c, is of particular interest; cf. Figure 4. This observation provides definite evidence that the Debye–Waller factors for the two phases, high-spin $^5T_2$ and low-spin $^1A_1$, are different. If no difference between $-\ln f_{^5T_2}$ and $-\ln f_{^1A_1}$ were involved, the curve for the temperature variation of $-\ln(\sum t_i)$ should be a straight line under the high-temperature approximation. Note that this conclusion directly follows from the Mössbauer effect areas and is not subject to any additional assumptions or approximations. The different Debye–Waller factors demonstrate that the mean-square amplitudes are different for those localized vibrations of the Fe(bts)$_2$(NCS)$_2$ molecular unit which are specifically associated with the ground states $^5T_2$ and $^1A_1$, and this is a consequence of the differing geometry, particularly the different Fe–N distances and bond angles of the molecules in the two spin isomers. These differences have been reported for the first time for [Fe(bpy)$_2$(NCS)$_2$], polymorph II[26] (bpy = 2,2′-bipyridyl) where the average distances Fe–N($^5T_2$) = 2.14 Å (at 295 K) and Fe–N($^1A_1$) = 2.02 Å (at ~100 K) suggested a difference in the Fe–N bond length of 0.12 Å. More recently, multiple-temperature X-ray investigations by counter methods provided more accurate results for a number of iron(II) compounds which show spin transitions of the continuous type. The studies include [Fe(2-pic)$_3$]Cl$_2$·C$_2$H$_5$OH,[27,28] [Fe(2-pic)$_3$]Cl$_2$·CH$_3$OH[27] and [FeCl$_2$(dppen)$_2$]·2(CH$_3$)$_2$CO[29] (where dppen = *cis*-1,2-bis(diphenylphosphino)ethylene, Ph$_2$PCH═CHPPh$_2$). Thus, e.g., the average bond lengths in [Fe(2-pic)$_3$]Cl$_2$·C$_2$H$_5$OH[28] are Fe–N($^5T_2$) = 2.195 Å and Fe–N($^1A_1$) = 2.013 Å, the Fe–N bond being shorter in the $^1A_1$ state by about 0.18 Å. A particularly large change of bond length has been found in [FeCl$_2$(dppen)$_2$]·2(CH$_3$)$_2$CO, where Fe–P($^5T_2$) = 2.584 Å (at 295 K) and Fe–P($^1A_1$) = 2.301 Å (at 130 K), thus giving for the difference of Fe–P bond lengths about 0.28 Å.

There is a considerable difference in the values of $\partial(\delta^{IS})/\partial T$ which implies that, at any temperature T, the mean-square velocity of the resonating nucleus is significantly different for the two spin isomers, high-spin $^5T_2$ and low-spin $^1A_1$, of [Fe(bts)$_2$(NCS)$_2$]. This is another direct consequence of the change in Fe–N bond distances on spin transition. The different contribution by the second-order Doppler effect provides additional support for the suggested difference in Debye–Waller factors of the two spin isomers since, in the harmonic approximation, these two quantities are directly correlated.[30] Thus, for molecular crystals, both recoil-free fraction and second-order Doppler shift are determined by two types of vibrations:[31] (i) intramolecular vibrations of higher frequency which are due to the motion of the iron ion within the molecule (optical branch); (ii) intermolecular vibrations of lower frequency which are due to the motion of the entire molecule within the lattice (acoustical branch). The Mössbauer fraction is more sensitive to the lower lattice frequencies, whereas the second-order Doppler shift is determined essentially by the higher frequencies. However, in determining the value of the recoil-free fraction for molecular crystals, the contribution of intramolecular vibrations cannot be ignored. For high-spin ⇌ low-spin transitions of the continuous type, as in [Fe(bts)$_2$(NCS)$_2$], the two spin isomers of the molecule are almost randomly distributed within the same lattice. Therefore, the intermolecular vibrations are expected to be similar, whereas intramolecular vibrations will be different.[32–34] Any attempt at the estimation of individual Debye–Waller factors for continuous high-spin ⇌ low-spin transitions will then be inaccurate, if proper consideration of the two types of vibration has not been introduced. In particular, if individual Debye–Waller factors should be determined over the spin transition region, the simplified approach based on the high-temperature approximation (method II of the Appendix) may not be applicable.

Suggestive of the mechanism of the spin transition in [Fe(bts)$_2$(NCS)$_2$] is the behavior of the difference in absorber line widths, $\Gamma_{^5T_2}{}^{abs} - \Gamma_{^1A_1}{}^{abs}$; cf. Figure 3. This quantity is seen to increase with increasing temperature difference from T_c, which shows that the line width of the minority constituent is also increasing. It seems that this finding can be explained only by a distribution of values for the quadrupole splitting ΔE_Q and/or the isomer shift δ^{IS} for the minority constituent, the former being the more important. This, in turn, suggests that the transformation, from the majority into the minority constituent, proceeds by way of a nucleation mechanism with a rather wide distribution of nuclei. Note that the experimental uncertainty is increasing with the distance from T_c, subject to the fitting error of the minority spectrum, although the significance of the results is not affected by this circumstance.

The above conclusion is supported by the finding, also illustrated by Figure 3, that the temperature dependence of ΔE_Q for the high-spin $^5T_2$ isomer is different above and below T_c. This again demonstrates that different Mössbauer characteristics are obtained, depending on whether, at the particular temperature, the $^5T_2$ isomer of the [Fe(bts)$_2$(NCS)$_2$] complex is incorporated into the majority or into the minority constituent.

Of considerable importance is the fact that, in X-ray diffraction, only a continuous shift of Bragg reflections with temperature is observed in the region around T_c; cf. Figure 5. The resulting shift of lattice spacings parallels that obtained for the high-spin fraction $n_{^5T_2}$ (cf. Figure 6) and thus demonstrates consistency of the X-ray diffraction measurements with the results of ^{57}Fe Mössbauer spectroscopy. It should be noted that, in compounds showing a spin transition of the discontinuous type, individual diffraction patterns for the two phases, $^5T_2$ and $^1A_1$, have been observed,[8,9,11,12] their relative intensities being a function of temperature. The only reasonable interpretation of the present results which may be suggested is based on the distribution of the two spin isomers. Thus, if a wide distribution of the minority constituent within the majority constituent is assumed, a single X-ray diffraction pattern will be indeed obtained, provided that any domains formed within the minority constituent do not approach the critical size which is required in order to produce an individual diffraction pattern. If, on the other hand, a narrow distribution of the minority constituent, accompanied by a pronounced domain formation, is assumed, different and individual diffraction patterns for the two phases will be observed. Moreover, it has been noted that, within experimental uncertainty, the line widths of the Bragg reflections for [Fe(bts)$_2$(NCS)$_2$] are constant at all temperatures studied. This finding likewise rules out the possibility of a significant domain formation by either of the two spin isomers.

The results collected for [Fe(bts)$_2$(NCS)$_2$] thus indicate that the two constituents, high-spin $^5T_2$ and low-spin $^1A_1$, show a behavior which is similar to that of a solid solution of two components. It is well-known that these solid solutions are stable only if certain specific conditions are met: (i) the crystal structure of both pure phases should be the same; (ii) the atomic radii of the involved atoms should not differ by more than about 15%; (iii) the distribution of the two phases should be at random.

The above assumptions seem to be consistent with the results of the present study on [Fe(bts)$_2$(NCS)$_2$]. In addition, X-ray structure studies on several iron(II) compounds which are showing a spin transition of the gradual type demonstrate[27–29] that the space

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Table II. Effective Thickness t_i, $i = {}^1A_1, {}^5T_2$, and Estimated Values of High-Spin Fraction $n_{^5T_2}$ and Recoil-Free Fractions f_i Obtained by an Iterative Procedure

T, K	$t_{^1A_1}$	$t_{^5T_2}$	$n_{^5T_2}$	$f_{^1A_1}$	$f_{^5T_2}$
103.1	0.025	0.899	0.046	0.386	0.465
107.5	0.016	0.859	0.048	0.361	0.439
117.2	0.032	0.804	0.060	0.341	0.422
131.6	0.029	0.772	0.033	0.319	0.405
141.6	0.025	0.693	0.050	0.281	0.363
154.2	0.032	0.622	0.070	0.251	0.333
166.6	0.024	0.566	0.069	0.221	0.300
177.4	0.033	0.542	0.069	0.213	0.295
188.9	0.044	0.484	0.104	0.194	0.274
198.8	0.057	0.423	0.157	0.176	0.252
206.5	0.089	0.364	0.254	0.170	0.247
212.0	0.109	0.298	0.352	0.155	0.229
220.0	0.153	0.219	0.518	0.150	0.224
227.4	0.185	0.137	0.683	0.138	0.208
235.2	0.191	0.091	0.771	0.125	0.192
238.7	0.192	0.083	0.794	0.123	0.184
247.7	0.180	0.063	0.819	0.110	0.173
256.4	0.173	0.052	0.847	0.103	0.164
264.4	0.158	0.045	0.849	0.092	0.149
272.7	0.145	0.037	0.847	0.083	0.137
281.5	0.135	0.037	0.845	0.079	0.131
291.5	0.118	0.025	0.848	0.066	0.113
229.3	0.185	0.129	0.699	0.135	0.205
223.1	0.165	0.168	0.603	0.139	0.208
212.8	0.110	0.315	0.344	0.165	0.243

group for the high-spin $^5T_2$ and the low-spin $^1A_1$ phase in these compounds is identical. Moreover, observed Fe–ligand bond distances[26–28] suggest that the change of the Fe ionic radius on spin transition does not exceed the stated limit. For the particular example of $[Fe(bpy)_2(NCS)_2]$,[26] this fact has been demonstrated previously, employing the Goldschmidt ionic radius[35] for the Fe^{2+} ion as a basis.

Conclusions

In view of the results obtained in the present and some earlier studies,[8,9,11,12] it seems that there exists a fundamental difference between the two types of high-spin ⇌ low-spin transitions:

(i) Transitions of the *discontinuous type* arise for compounds with strong cooperative interaction. Pronounced domain formation by the minority phase is encountered, and therefore an individual X-ray diffraction pattern for that phase is formed. Due to the domain formation, the transition completes within a very narrow temperature range and is associated, in general, with a crystallographic phase change. Any observed hysteresis effects are a consequence of the domain formation.

(ii) Transitions of the *continuous type* are formed for compounds with weak cooperative interaction. In this case, a wide distribution of nuclei for the minority constituent is encountered, and thus no separate X-ray diffraction pattern for that constituent is formed. The two spin isomers form a solid solution within the same lattice, a crystallographic phase change is not involved, and thus the transition extends over a wide range of temperature. However, similar to (i), the transition is associated with a change of volume, and therefore a continuous variation of the lattice spacings is encountered as the transition progresses. Since domain formation is essentially absent, hysteresis effects are not observed.

In both cases, the transition may be initiated similarly at defect sites, on the surface, at grain boundaries and other locations of relatively high energy. As a consequence of the different Fe–N bond distances and the associated changes of intramolecular vibrations, a difference in the recoil-free fraction for the two spin isomers is found, irrespective of the type of transition.

The apparent change of a discontinuous type of transition into quasi-continuous behavior on grinding or doping is a consequence of the smaller size of domains which result during that process. Nonetheless, the essential features of the first-order transition such as hysteresis effects and other manifestations of the domain formation are retained.

It thus seems established, on the basis of experimental results, that the mechanism of the two types of high-spin ⇌ low-spin transitions shows characteristic differences. Theoretical models which include the formation of both gradual and abrupt spin transitions on the change of a single parameter[15–20] should be therefore considered with caution. It seems that separate theoretical treatments for the two types of transition will be rather required. On the basis of the present results, it is expected that an Ising-type model[15] for example should be applicable to gradual transitions, whereas domain models for example should account for abrupt transitions. From the theoretical studies which have been advanced so far, this is not clearly evident.

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Appendix

There are two methods for the detailed determination of individual Debye–Waller factors, $-\ln f_{^5T_2}$ and $-\ln f_{^1A_1}$, which we have used in earlier studies:

Method I. This approach[14] is based on the determination of $n_{^5T_2}$, as a function of temperature, from experimental magnetic susceptibility data. From the values of $n_{^5T_2}$ and the values for $t_{^5T_2}$ and $t_{^1A_1}$, the Debye–Waller factors follow via eq 2. The complications of this method arise due to the uncertainties in the assumed values of the effective magnetic moment μ_{eff} for the *pure* ground states, $^5T_2$ and $^1A_1$, which are required. Additional sources of error are various experimental factors, such as differences in temperature determination for the two sorts of measurement or differences in sample packing, which are affecting the magnetic data in a different way than the results of Mössbauer measurements, the latter via the quantity d; cf. eq 2.

Method II. In this method,[11] it is assumed that the high-temperature approximation for the Debye–Waller factor is applicable to molecular crystals and that both $f_{^5T_2}$ and $f_{^1A_1}$ are continuous functions throughout the spin transition region. In this case, one can write

$$f_{^5T_2} = e^{-HT} \qquad f_{^1A_1} = e^{-LT} \tag{A1}$$

where H and L are characteristic constants for the two types of lattice. From eq 2 one then obtains

$$\ln t_{^5T_2} = \ln d + \ln n_{^5T_2} - HT \tag{A2}$$

$$\ln t_{^1A_1} = \ln d + \ln (1 - n_{^5T_2}) - LT$$

Thus, for any spectrum recorded at a particular temperature T_k one may write

$$H_k = -\frac{1}{T_k}[\ln (t_{^5T_2}{}^k + t_{^1A_1}{}^k e^{-(\bar{H}-\bar{L})T_k}) - \ln d] \tag{A3}$$

$$L_k = -\frac{1}{T_k}[\ln (t_{^1A_1}{}^k + t_{^5T_2}{}^k e^{-(\bar{H}-\bar{L})T_k}) - \ln d]$$

In eq A3, $\bar{H} = {}^1/_n \sum H_k$ is the average for n measurements and similarly $\bar{L} = {}^1/_n \sum L_k$. Equation A3 may be solved by an interation procedure on condition that $\sum(\bar{H} - H_k)^2$ or $\sum(\bar{L} - L_k)^2$ is minimum. The resulting values of $\bar{H}$ and $\bar{L}$ in conjunction with d determine the unknown quantities $f_{^5T_2}$, $f_{^1A_1}$ and $n_{^5T_2}$ according to eq 2.

Method II has been used in the analysis of the Mössbauer effect measurements of the present study, the detailed results being collected in Table II. As expected, the Debye–Waller factors $-\ln f_{^5T_2}$ and $-\ln f_{^1A_1}$ show a linear dependence on temperature with the slopes $\bar{H} = 0.0089$ and $\bar{L} = 0.0071$. The iterative procedure yields, in addition, the high-spin fraction $n_{^5T_2}$ which is displayed, as a function of temperature, in Figure 2. It is evident that the functions $f_{^5T_2}$, $f_{^1A_1}$, and $n_{^5T_2}$ do show the expected behavior. However, due to the limitations of the employed method, any more general conclusions from the results should be considered with caution. For more details refer to the Discussion section above.

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