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Effect of a Simultaneous Change of Temperature and Pressure on the Spin-State Transition in Bis(thiocyanato)bis(2,2′-bi-2-thiazoline)iron(II)

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Spin-state transitions in metal compounds are well-known to be induced by changes of temperature[4,5] or pressure,[6,7] some more complicated phenomena being associated with the irradiation of light[8] or the gradual dilution of the metal ion.[9,10] Most of the reported transitions have been studied as a function of temperature, although pressure induced spin-state transitions are also well documented. The combined-effect of temperature and pressure has received only little attention thus far.[11] This is rather surprising given the promising potential of these compounds in molecular electronics.[12]

One of the few examples where a study of the pressure dependence of a thermally induced spin-state transition has been performed are the compounds $[Fe(phy)_2](BF_4)_2$ and $[Fe(phy)_2](ClO_4)_2$ where phy = bis(1,10-phenanthroline-2-carbaldehyde phenylhydrazone.[13] A flattening of the hysteresis loop has been generally observed, both the hysteresis width ΔT_c and the residual high-spin fraction n_{HS}^{res} assuming higher values with an increase of pressure.

The present study has been initiated in order to show whether or not the above results are of more general applicability. To this end, the effect of pressure on the spin-state transition in $[Fe(bt)_2(NCS)_2]$ and its hysteresis[14] have been studied, where bt = 2,2′-bi-2-thiazoline.

Experimental Section

Materials. The ligand 2,2′-bi-2-thiazoline was prepared by the method of Tomalia and Paige[15] by the reaction of the condensation product of 2-aminoethanol and dithiooxamide with thionyl chloride. The iron(II) complex was obtained following Bradley et al.[16] using iron metal powder enriched to >95% with the isotope ^{57}Fe. The sample purity was checked by elemental analysis for C, H, N, and Fe and by IR as well as ^{57}Fe Mössbauer spectroscopy.

Measurements. ^{57}Fe Mössbauer spectra were obtained as described previously.[17] For measurements under an applied pressure, the enriched sample was pressed between two disks of boron carbide, B_4C, with use of an indium metal gasket. The assembly was enclosed in a tempered steel chamber, and a constant pressure was applied with a calibrated hydraulic press. The sample was maintained at a particular pressure by a suitable locking device and placed in a custom-made superinsulated cryostat. Temperatures between 80 and 300 K were monitored by means of a calibrated iron vs constantan thermocouple and a cryogenic temperature controller (Lake Shore Cryogenics DRC-91 CA). The temperature stability was ±0.10 K. The resulting data were corrected for the nonresonnant background of the γ-rays and the spectra were fitted employing the procedure of the convolution integral.[13] In order to account for possible line broadening effects, the Voigt profile,[18] which is an approximation of a convolution of a Lorentz function and a Gauss function, was used for both the source and the absorber function. The form factor α varies thereby between the value 0.5 for a pure Gaussian profile and 1.0 for a Lorentzian profile. For the absorber function, thus a HS line width $\Gamma_{HS} = 0.150$ mm s^{-1} and a LS line width $\Gamma_{LS} = 0.141$ mm s^{-1} were obtained. For the absorber and the source function, a Gaussian contribution equal to zero was obtained (i.e. $\alpha = 1.0$) and the source line width $\Gamma_s = 0.098$ mm s^{-1} (as given by the manufacturer Amersham) was used.

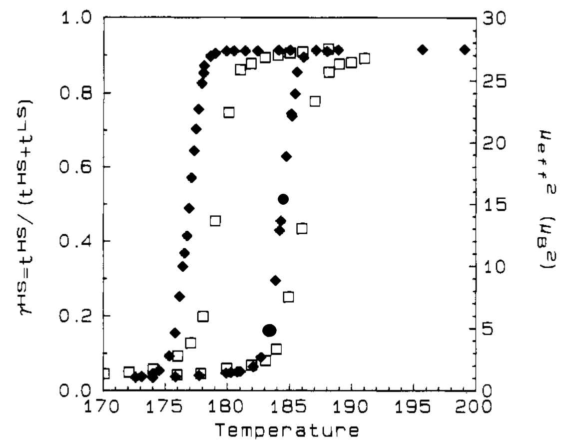

Figure 1. Temperature dependence of γ_{HS} at atmospheric pressure from ^{57}Fe Mössbauer effect measurements (□) and of μ_{eff}^2 from magnetic susceptibility measurements (◆) at the spin-state transition in $[Fe(bt)_2(NCS)_2]$.

The fit produces values of the effective thickness

$$t^{HS} = f^{HS} n_{HS} \qquad t^{LS} = f^{LS}(1 - n_{HS}) \tag{1}$$

the HS fraction being obtained as

$$n_{HS} = t^{HS}/[(f^{HS}/f^{LS})t^{LS} + t^{HS}] \tag{2}$$

Since, in the present study, the Debye-Waller factors f^{HS} and f^{LS} are dependent on both pressure and temperature, the quantity

$$\gamma_{HS} = t^{HS}/(t^{HS} + t^{LS}) \tag{3}$$

rather than n_{HS} has been derived from the experimental data. From the experimental values of $(t^{HS} + t^{LS})$ above and below the transition region, the ratio f^{HS}/f^{LS} at 182.5 K has indeed been found to vary between 1.40 at ambient pressure and 1.14 at 1.9 kbar. This finding shows clearly that the Debye-Waller factors f^{HS} and f^{LS} are considerably different. As a consequence, the results of various authors based on the assumption that $f^{HS} = f^{LS}$ are open to question.

Results

The results of measurements of the temperature-induced spin-state transition at atmospheric pressure as obtained for the present sample are displayed in Figure 1. Values derived from Mössbauer spectra are shown in terms of the quantity γ_{HS}, values determined from magnetic susceptibility measurements are shown as the effective magnetic moment squared μ_{eff}^2. According to the Mössbauer spectra, the transition takes place at $T_c^{\uparrow} = 186.3$ K

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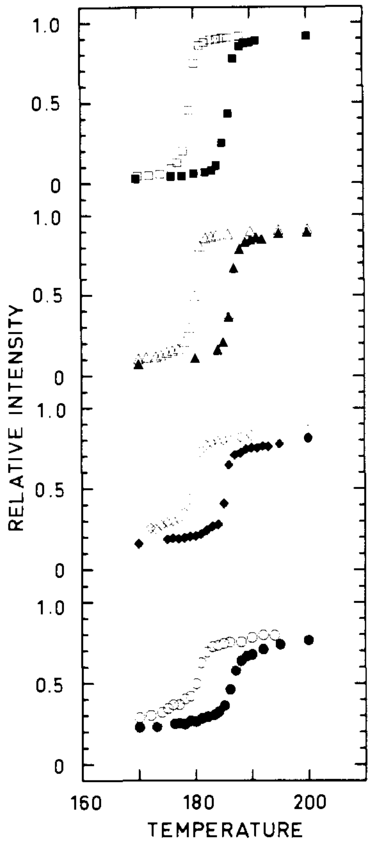

Figure 2. Temperature dependence of γ_{HS} at the spin-state transition in $[Fe(bt)_2(NCS)_2]$ from ^{57}Fe Mössbauer effect measurements for pressures of 0.001, 0.65, 1.25, and 1.90 kbar (from top to bottom). Filled symbols are for increasing temperatures; open symbols for decreasing temperatures.

Table 1. Characteristic Data for the Spin-State Transition in $[Fe(bt)_2(NCS)_2]$ under Applied Pressure[a]

p (kbar)	$T_c^{\uparrow}$ (K)	$T_c^{\downarrow}$ (K)	ΔT_c (K)	γ_{HS}^{res}
0.001	186.3	179.2	7.1	0.02
0.65	186.4	180.2	6.2	0.09
1.25	185.3	179.4	5.9	0.21
1.90	186.2	180.5	5.7	0.23

[a] Values of $T_c^{\uparrow}$ and $T_c^{\downarrow}$ are ±0.4 K, values of ΔT_c are ±0.3 K.

and at $T_c^{\downarrow} = 179.2$ K for increasing and decreasing temperatures, respectively. The different transition temperatures for the two series of data are due to the different method of temperature measurement. The hysteresis shows the same width of $\Delta T_c = 7.1$ K in both cases.

The effect of pressure on the spin-state transition is demonstrated best if the results are again displayed in terms of the hysteresis loops. Figure 2 shows the hysteresis curves obtained on the basis of Mössbauer effect measurements for the applied pressures of 0.001, 0.65, 1.25, and 1.90 kbar, with 0.001 kbar corresponding to atmospheric pressure. As evident from the figure, the hysteresis shows a characteristic flattening with increasing pressure. The resulting values of the transition temperatures $T_c^{\uparrow}$ and $T_c^{\downarrow}$ as well as those of the hysteresis width $\Delta T_c = T_c^{\uparrow} - T_c^{\downarrow}$ and the residual fraction γ_{HS}^{res} are listed in Table 1. Here, values of $T_c^{\uparrow}$ and $T_c^{\downarrow}$ have been determined from the maxima of the derivative curves.

Figure 3 shows Mössbauer spectra for different pressures at the two temperatures, 182 and 177 K, which were obtained in the cooling mode and are close to the observed transition temperatures. At 182 K, the quantity γ_{HS} corresponding to the HS fraction decreases for increasing pressures from $\gamma_{HS} = 0.88$ to 0.70, whereas at 177 K, an increase from $\gamma_{HS} = 0.13$ to 0.37 is observed; cf. Table 2. The results show that the transition can be pressure induced at these temperatures, although the value of the transition pressure cannot be reliably estimated from the data. The increase of γ_{HS} with increasing pressure demonstrates that the HS → LS conversion gets less and less complete, i.e. that the residual fraction n_{HS}^{res} rises with pressure; cf. Figure 2.

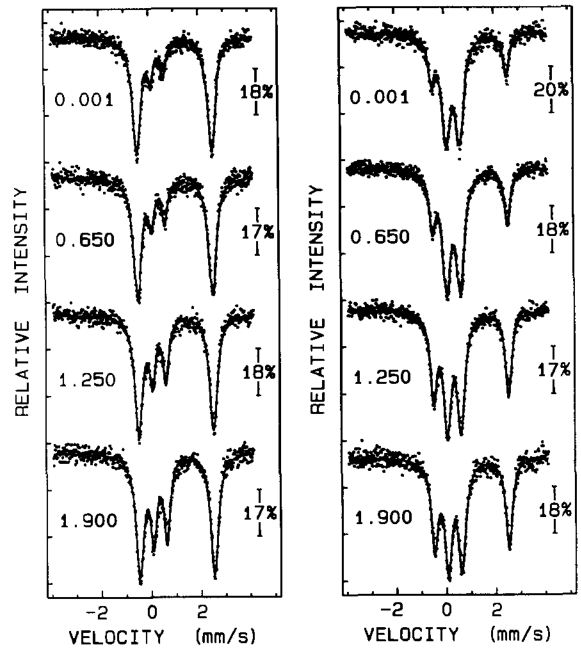

Figure 3. ^{57}Fe Mössbauer effect spectra of $[Fe(bt)_2(NCS)_2]$ for the temperatures of 182 K (left) and 177 K (right) obtained in the decreasing temperature mode. The spectra are for the pressures 0.001, 0.65, 1.25 and 1.90 kbar, from top to bottom, respectively.

Table 2. Values of γ_{HS} for $[Fe(bt)_2(NCS)_2]$ Resulting at 182 K and at 177 K for Different Applied Pressures[a]

T = 182 K		T = 177 K	
p (kbar)	γ_{HS}	p (kbar)	γ_{HS}
0.001	0.88	0.001	0.13
0.65	0.86	0.65	0.17
1.25	0.77	1.25	0.36
1.90	0.70	1.90	0.37

[a] Values of γ_{HS} are ±0.01, pressures p are ±0.05 kbar.

Several series of measurements have been performed, and after each series with increasing pressure, the pressure was completely released. Within experimental uncertainty, the original hysteresis loop was always reproduced.

Discussion

At atmospheric pressure, the compound $[Fe(bt)_2(NCS)_2]$ shows a temperature-induced spin-state transition, the transition temperatures for increasing and decreasing temperatures having been determined previously[14] as $T_c^{\uparrow} = 181.9$ and $T_c^{\downarrow} = 172.3$ K, respectively. The resulting hysteresis is characterized by a width of $\Delta T_c = 9.6$ K, in the present sample it has been found $\Delta T_c = 7.1$ K. The first-order character of the transition has been established by the abrupt nature of the transition and the recent heat capacity measurements[19] which produced values of the transition enthalpy $\Delta H = 9.54 \pm 0.5$ kJ mol^{-1} and the transition entropy $\Delta S = 54.4 \pm 3.0$ J mol^{-1} K^{-1}. If the Frenkel theory of heterophase fluctuations is applied to these results, a domain size of $n \simeq 51$ molecules is obtained.

With application of pressure, transition temperatures show no noticeable change within the range 0.001–1.90 kbar. On the other hand, the hysteresis width decreases significantly from $\Delta T_c = 7.1$ K at atmospheric pressure to $\Delta T_c = 5.7$ K at 1.9 kbar.

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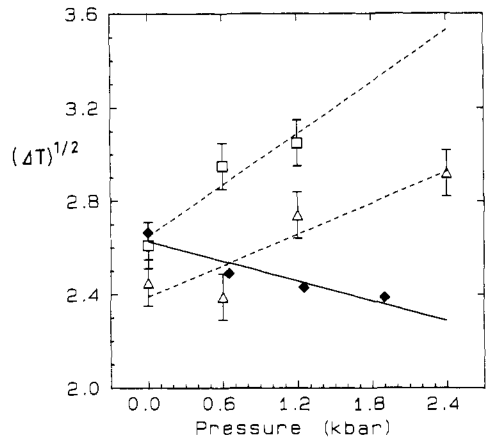

Figure 4. Hysteresis width $(\Delta T_c)^{1/2}$ as a function of the applied pressure p for $[Fe(phy)_2](BF_4)_2$ (△), $[Fe(phy)_2](ClO_4)_2$ (□) and $[Fe(bt)_2(NCS)_2]$ (◆). Error bars are indicated. The errors for the black points (◆) are all identical and are indicated therefore only for the point at 0 kbar. Straight lines are not fitted.

Within the accuracy of measurement the decrease of $(\Delta T_c)^{1/2}$ with pressure is linear. A linear relationship has indeed been proposed previously by Das and Ghosh[20] who used an ansatz of the Landau theory. Thus it has been shown that

$$d(\Delta T_c)^{1/2}/dp = -\beta/(3KC)^{1/2} \qquad (4)$$

Since all quantities on the right hand side of eq 4 are constant, a linear relation between the square root of the hysteresis width $(\Delta T_c)^{1/2}$ and pressure p is proposed. Evidently, both an increase and a decrease of $(\Delta T_c)^{1/2}$ are possible. Figure 4 shows the pressure dependence of $(\Delta T_c)^{1/2}$ for the three compounds so far studied. Whereas an increase of $(\Delta T_c)^{1/2}$ with increasing pressure has been observed for $[Fe(phy)_2]X_2$ ($X = BF_4$, ClO_4), a decrease is found for the present case of $[Fe(bt)_2(NCS)_2]$. Within the realm of the applied model, the studied first-order transition should transform into a second-order transition (for $\beta > 0$) or not at all (if $\beta \leq 0$). The increase of residual fraction n_{HS}^{res} at the lowest temperatures studied is evident from Figure 2 and the data of Table 1. Similar to the results obtained for $[Fe(phy)_2]X_2$ ($X = BF_4$, ClO_4), the increase of n_{HS}^{res} may be explained by the assumption of decreasing size of the cooperative region with increasing pressure.

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