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# Lamb Mössbauer factor of the spin crossover compound [Fe(BPTN)(NCS)<sub>2</sub>]

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**Abstract.** The spin crossover transition curve of the compound [Fe(BPTN)(NCS)<sub>2</sub>] (BPTN = N,N'-bis(2-pyridylmethyl)-1,3-propanediamine) was measured by Mössbauer spectroscopy and susceptibility measurements. The compound was prepared by two different methods yielding a fine powder (a) and single crystals of ~ 0.5 mm in size (b). The transition temperatures  $T_{1/2}$  of the gradual transitions are 182 K (a) and 186 K (b). Within experimental accuracy the transition curves derived from the fractional absorption areas of the Mössbauer spectra are the same as derived from susceptibility measurements so that there is no indication for different Lamb Mössbauer factors of the high-spin (HS) and low-spin (LS) states as reported in the literature. The observation of quite different Debye temperatures  $\Theta_D$  at temperatures where the compounds are completely converted to the HS and LS state is discussed.

## 1. Introduction

The Lamb Mössbauer factor in spin crossover compounds has been subject to controversial discussions in the literature. For several compounds, comparing results from susceptibility and Mössbauer measurements, a significantly larger Lamb Mössbauer factor for the complex molecule in the low-spin ( $f_{LS}$ ) than in the high-spin state ( $f_{HS}$ ) was reported, while for compounds studied in our laboratory such differences could not be observed. We have recently prepared and remeasured the spin crossover compound [Fe(TPA)(NCS)<sub>2</sub>] (TPA = tris(2-pyridylmethyl)) the  $f$ -factors of which were determined by Yousif *et al* to be very different for the two spin states [1]. The transition temperatures determined from the area fractions of the HS and LS states differed considerably (~ 10 K) from that determined by susceptibility measurements. We found, however, the  $f$ -factors in the HS and LS state of this compound to be the same within experimental error [2]. It turned out that a meaningful evaluation of the  $f$ -factors requires well crystallized samples. The effect of different  $f$ -factors in the two spin states on the transition curve becomes larger the more gradual the transition and the higher the transition temperature. The first statement is obvious as for the extreme case of an abrupt transition, where the HS fraction changes nearly from zero to unity at the transition temperature, the  $f$ -factors play no role. The second statement is based on the fact that the ratio of different  $f$ -factors increases with increasing temperature. Since the compounds studied so far in our laboratory have low transition temperatures around 100 K we could have missed the effect of different  $f$ -factors on the transition curve derived from the area fractions. Therefore, we decided to remeasure the title compound also described in the publication of Yousif *et al* [1] as exhibiting significantly different  $f$ -factors in the two spin states and which has a very gradual transition at a high temperature of 180 K.

## 2. Preparation

Preparation of the ligand N,N'-bis(2-pyridylmethyl)-1,3-propanediamine (BPTN) was carried out as follows. The ligand was prepared by a modification of the methods of Toftlund *et al* [3,4] and Newkome *et al* [5]. Under an argon atmosphere, a solution of distilled 2-pyridinecarbaldehyde (Aldrich) (10.5 g, 98 mmol) in absolute ethanol (10 ml) was slowly over a period of 1 h added to a rapidly stirred solution of 3.7 g (50 mmol) 1,3-diaminopropane (Aldrich) in absolute ethanol (10 ml). Then the mixture was refluxed for 1 h. After cooling to room temperature the solution was evaporated in a vacuum to give a dark red oily residue, which was dissolved in 150 ml of absolute ethanol. 5 g (132 mmol) NaBH<sub>4</sub> were added to this solution and the mixture was refluxed under stirring for 24 h. After the mixture was cooled to room temperature 15 ml of concentrated HCl was added and the solvents were evaporated. The red-brown residue of crude ligand was dried in a vacuum for 1 h and then aqueous HCl (50 ml, 2 mol l<sup>-1</sup>) was added. The aqueous solution was washed with CHCl<sub>3</sub> (2 × 50 ml) and after this the pH was adjusted to 12 with concentrated NaOH. The ligand was extracted with CHCl<sub>3</sub> (5 × 50 ml). The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated in a vacuum to a red-brown oil. Fractionated distillation in a high vacuum (2 × 10<sup>2</sup> mbar) gave 7.2 g (57%) of a yellow oil (BP = 150–1550 °C) characterized by IR and <sup>1</sup>H-NMR spectroscopy. The preparations of the compound Fe(BPTN)(NCS)<sub>2</sub> were done in a glove box under an argon atmosphere to avoid oxidation of the Fe(II).

### 2.1. Powder sample

This sample was obtained according to the method of Toftlund *et al* [4]. A solution of 1.4 g (5 mmol) FeSO<sub>4</sub>·7H<sub>2</sub>O in water (20 ml) and a solution of 1.28 g (5 mmol) BPTN in ethanol (20 ml) were both heated to approximately 500 °C. The ligand solution was added with stirring to the iron(II) solution, immediately followed by a solution of 1 g (10 mmol) KSCN in water (2 ml). A green precipitate was formed instantly. The mixture was heated for 2–3 min and then slowly cooled to room temperature. The precipitated green complex was filtered off and washed twice with water and once with ethanol. Drying in a vacuum yielded 1.8 g (84%) of a green powder, which was stored under argon. Characterization was done by elemental analysis and IR spectroscopy.

### 2.2. Crystalline sample

A sample with small crystals was obtained by some modifications of the above method. To a boiling solution of 545 mg (1.95 mmol) FeSO<sub>4</sub>·7H<sub>2</sub>O in water (100 ml) was added to a hot solution of 500 mg (1.95 mmol) BPTN in ethanol (100 ml) with stirring, immediately followed by 380 mg (3.90 mmol) KSCN in water (10 ml). The resulting green solution was refluxed for some minutes and then slowly cooled to room temperature. Small green plate-like crystals were filtered off, washed with water and ethanol and dried in a vacuum (400 mg, 48%). Elemental analysis and IR spectroscopy were used for characterization.

## 3. Measurements and results

The Mössbauer spectra were recorded in conventional transmission geometry with a <sup>57</sup>Co/Rh source (at RT). A selection of spectra of the samples under study is shown in figure 1. The spectra were evaluated using the transmission integral in order to take into account thickness effects. The powder sample contains an impurity of Fe(II) in the high-spin state of 8%

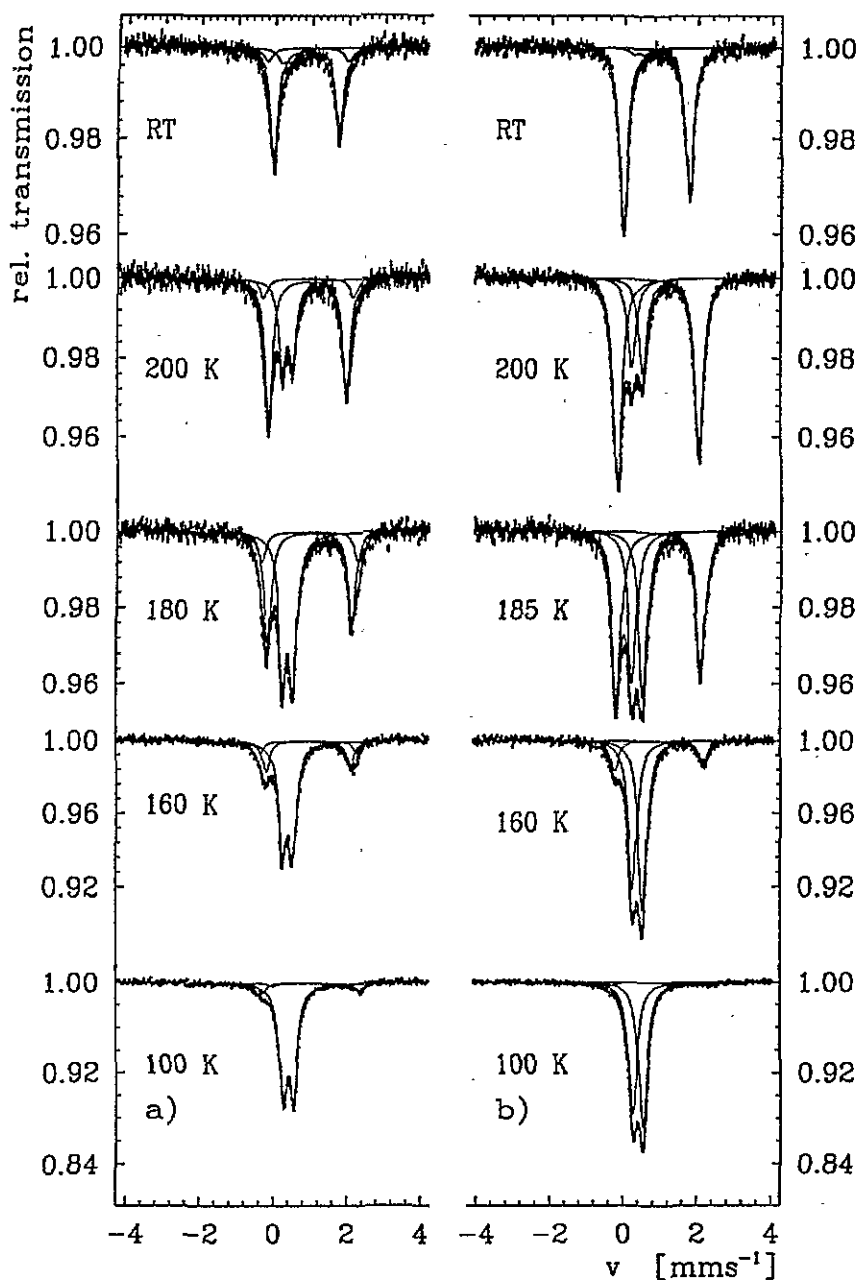


Figure 1.  $^{57}\text{Fe}$  Mössbauer spectra of the spin crossover compound  $[\text{Fe}(\text{BPTN})(\text{NCS})_2]$ . Sample a is a fine powder sample and sample b is crystalline as obtained from different preparation procedures. The solid lines indicate the subspectra fitted to each spectrum.

with a quadrupole splitting of  $2.38 \text{ mm s}^{-1}$  which is appreciably larger than  $1.92 \text{ mm s}^{-1}$  of the HS state taking part in the spin transition. The quadrupole splitting of the LS state at 100 K is  $0.28 \text{ mm s}^{-1}$ . The crystalline sample b has the same Mössbauer parameters but no Fe(II) impurity. The Debye-Scherrer photographs of both compounds are also the same,

so that there is no doubt that the two preparations differ only in their degree of purity. The transitions are not complete at RT: there is 8% LS in the powder sample and 3% LS in the crystalline one, whereas both are complete at low temperatures.

The magnetic susceptibilities were measured with a Foner magnetometer. The data were fitted by a sum of three susceptibilities

$$c(T) = \gamma_{\text{HS}}(T)c_{\text{HS}}(T) + (1 - \gamma_{\text{HS}}(T))c_{\text{LS}} + c_{\text{R}}(T) \quad (1)$$

where  $c_{\text{HS}}(T) = C_{\text{HS}}/T$ ,  $c_{\text{LS}}$  is independent of  $T$  and  $c_{\text{R}}(T) = C_{\text{R}}/T$  is the residual HS of sample a. Taking a typically small value for  $c_{\text{LS}} = 2 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$  ( $\approx 10^{-2} c_{\text{HS}}(\text{RT})$ ),  $c_{\text{LS}}$  is obtained from  $c(T \leq 100 \text{ K})$  where  $\gamma_{\text{HS}} = 0$  and  $C_{\text{HS}}$ ,  $C_{\text{R}}$  from the high-temperature region ( $T \geq 240 \text{ K}$ ) taking as a first approximation for  $\gamma_{\text{HS}}(T)$  the HS area fraction of the Mössbauer spectra  $A_{\text{HS}}(T)/(A_{\text{HS}}(T) + A_{\text{LS}}(T))$ .  $C_{\text{HS}} = 3.19 \text{ K cm}^3 \text{ mol}^{-1}$  for sample a was smaller than  $3.55 \text{ K cm}^3 \text{ mol}^{-1}$  for the crystalline sample b). The larger value is attributed to the fact that the few single crystals in the sample holder are not randomly oriented as in the powder sample. The susceptibility data then determine according to (1)  $\gamma_{\text{HS}}(T)$  at each temperature over the whole temperature range. A statistical error cannot be attributed to the data, since  $c(T)$  is measured with large integration times. Systematic errors are of the order of 1%. In figure 2  $\gamma_{\text{HS}}(T)$  is plotted for both preparations: powder sample a (●) and crystalline sample b (○). The transition curve for the powder sample a is more gradual but the transition temperatures are almost the same. The results from the Mössbauer spectra are also plotted in figure 2 with the statistical errors of the fitted Mössbauer parameter. The area ratios  $A_{\text{HS}}(T)/(A_{\text{HS}}(T) + A_{\text{LS}}(T))$  of the spin changing molecules in the samples a (Δ) and b (+) agree well with  $\gamma_{\text{HS}}(T)$  obtained from the susceptibility data. Obviously the curves are the same within the experimental errors. The use of the area ratios in the high-temperature region ( $\geq 0.85$ ) for the HS fraction as a first approximation does not lead to inconsistencies and, therefore, the evaluation procedure cannot be improved. There is no significant shift of the transition temperatures obtained from the two measuring methods, in contrast to the results of Yousif *et al* [1].

#### 4. Discussion

There are several examples in the literature where authors have reported on different  $f$ -factors in the two spin states ([1] and references therein) based only on comparison with susceptibility data. Yousif *et al* actually investigated the title compound by three independent methods. The transition temperatures obtained from both  $c(T)$  and infrared optical absorption measurements (FTIR) of  $[\text{Fe}(\text{BPTN})(\text{NCS})_2]$  were in accordance with each other, but differed by 20 K from that derived from the area ratio  $A_{\text{HS}}(T)/(A_{\text{HS}}(T) + A_{\text{LS}}(T))$  of the Mössbauer spectra. Their second compound in that article,  $[\text{Fe}(\text{TPA})(\text{NCS})_2]$  (TPA = tris(2-pyridylmethylamine), shows an incomplete transition at low temperatures as well as at RT and the transition curves derived from susceptibility data and the area fraction of the Mössbauer spectra have very different shapes. These findings are in contrast to our own experience with  $f$ -factor studies of gradual transitions using Mössbauer and  $c(T)$  measurements. In the case of  $[\text{Fe}(\text{TPA})(\text{NCS})_2]$  we have shown that our preparations of this compound do not show discrepancies between the two measuring methods [2]. The statements concerning different  $f$ -factors in the two spin states of the title compound  $[\text{Fe}(\text{BPTN})(\text{NCS})_2]$  looked more reliable in the work of Yousif *et al*. The measurements on the two preparations presented in this work, however, throw some light on the reason

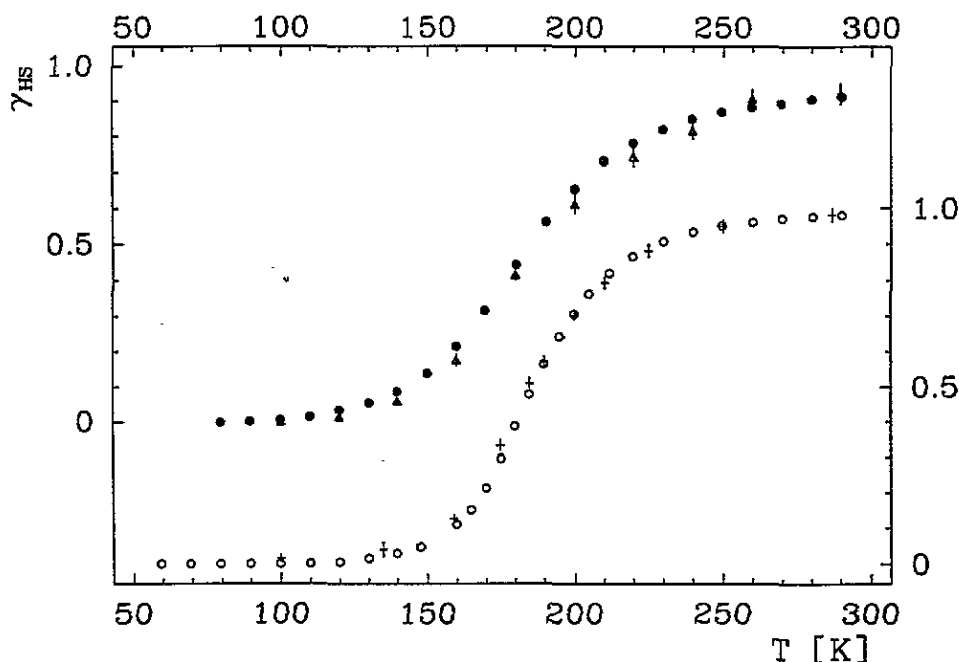


Figure 2. HS-LS conversion curve  $\gamma_{HS}(T)$  obtained from susceptibility data of the powder sample a (●) and crystalline sample b (○). The area ratios  $A_{HS}(T)/(A_{HS}(T) + A_{LS}(T))$  from the Mössbauer spectra of the spin changing molecule in the samples a (Δ) and b (+) compare well with the susceptibility data.

for our results, that do not indicate any difference between the  $f$ -factors of the spin states. It is well known that the spin transition characteristics are very sensitive to all kinds of lattice distortion [6] leading to incomplete transitions with a residual HS fraction at low temperatures and/or a residual LS fraction at high temperatures. We therefore used the same sample without grinding for susceptibility and Mössbauer measurements and found no difference in the results from both methods for each of these preparations. The possibility that Yousif *et al* prepared a sample which was different from ours is unlikely since our two preparations, although exhibiting different transition behaviour, have the same hyperfine parameters and powder x-ray photographs. A comparison of the hyperfine parameters with the preparation of Yousif *et al* is not possible. The only reported quadrupole splitting of the HS state is the one recorded at 4.2 K. Our preparations have complete transitions at low temperatures so that there is no HS doublet at all in the Mössbauer spectrum at 4.2 K. The transition curve of the powder sample a is remarkably flattened and has a high LS fraction (10%) at RT part of which may be residual, i.e. not participating in the spin transition. A residual LS fraction at high temperatures is indicative of a poor quality of the compound since the Boltzmann population saturates at a HS fraction very close to unity. The fact that the compound of Yousif *et al* shows a HS fraction of  $\sim 10\%$  at low temperatures and our compound, even the polycrystalline (a) sample, does not, makes it very likely that the quality of their compound was still poorer, which may be the reason for the observed discrepancies in the HS fractions determined by the different methods. Some reasons are given in the following.

The evaluation procedure in [1] is based on the fact that the slopes of  $\ln A(T)$  against

$T$  are different in the LS region at low temperatures and the HS region at high temperatures. The different slopes were then taken as representative for the temperature dependence of the  $f$ -factors in the LS and HS states. The origin of the different  $f$ -factors, however, has to be considered more closely. In molecular crystals the inter- and intramolecular vibrations are decoupled to a good approximation so that the  $f$ -factor can be written as a product of the lattice part  $f_l$  and a molecular part  $f_m$ :  $f = f_l f_m$ . Both parts may change with the spin state or with the fraction of molecules in each spin state. From the different intramolecular vibrations in the HS and LS states result different molecular  $f$ -factors:  $f_m^{\text{HS}}(T) \neq f_m^{\text{LS}}(T)$ . The change of the volume (1%–3%) and the shape of the molecule accompanying the spin transition change the factor  $f_l$ . It is found that the lattice expansion and also deformation is proportional to  $\gamma_{\text{HS}}$  [7], with the consequence that the Debye temperatures  $\Theta_{\text{D}}$  of the lattice well below (at  $\gamma_{\text{HS}} = 0$ ) and well above the transition temperature (at  $\gamma_{\text{HS}} \simeq 1$ ) are different. What really is observed depends on the manner in which the spin transition takes place. If the molecules with different spin states are randomly distributed over the crystal the long-wave phonons of the lattice determining the lattice part will depend on the average deformation as is observed by x-ray diffraction in the case of gradual transitions. The lattice part is then a function of  $\gamma_{\text{HS}}$  and the  $f$ -factors of the spin states are  $f^{\text{HS}}(T) = f_l(\gamma_{\text{HS}}(T)) f_m^{\text{HS}}(T)$  and  $f^{\text{LS}}(T) = f_l(\gamma_{\text{HS}}(T)) f_m^{\text{LS}}(T)$ . The fact that we need not differentiate between  $f^{\text{HS}}(T)$  and  $f^{\text{LS}}(T)$  means that the molecular parts are not sufficiently different to be observed by the spin transition. This effect was taken into account in the evaluation of  $f(T)$  in the spin crossover compound  $[\text{Fe}(\text{2-pic-ND})_3]\text{Cl}_2 \cdot \text{EtOD}$  [8]. If, however, the spin crossover molecules form clusters with different HS fractions, the  $f$ -factors for different clusters have to be considered. The evaluation procedure of Yousif *et al* is correct in two extreme cases: (i)  $f_l$  does not depend on the HS fraction and the difference is due to the molecular part, or (ii) the existing clusters are of 100% HS or 100% LS and the spin transition takes place by clusterwise conversion from one spin state to the other. The clusters have to be large enough (macroscopic) in order to meet the complete change of the Debye temperature. Such a picture can obviously be tested by metal dilution studies as carried out with other compounds [9] or by the following reasoning.

In figure 3 the logarithm of the  $f$ -factor of the crystalline sample b derived from the total area of the LS and HS resonance lines is plotted versus temperature. According to the arguments above the strong change of the slope of  $\ln f$  is due to the lattice contribution  $f_l$  which is a function of the HS fraction. For spin crossover compounds one typically observes that in the transition region the  $\ln f$  values are above the straight line fitted to the high-temperature data (figure 3). Arguing within the Debye approximation this observation indicates that  $\Theta_{\text{D}}$  depends on temperature.

Clear and direct experimental evidence for the existence of different  $f$ -factors in the HS and LS states arising from different intramolecular vibrations has been achieved by the LIESST effect (LIESST = light induced excited spin state trapping) [10]. At low temperatures ( $\leq 50$  K) the LS state is excited to the HS state by light and has sufficiently long lifetimes for a Mössbauer measurement. If this is done in a highly diluted mixed crystal such that the few spin changing complexes with  $^{57}\text{Fe}$  do not change the Debye temperature of the lattice the change of  $f_m$  by the different intramolecular vibration of the spin states can be measured at a given temperature. Such measurements have been performed on the system  $[\text{Fe}(\text{propyltetrazole})_6](\text{BF}_4)_2$  and will be published [11]. The  $f_m$  factors of the HS state after LIESST are smaller than for the LS state before LIESST. The difference is 4% at 50 K and is estimated to be 13% at 180 K, which is shown to be not sufficient to be observed in a gradual spin transition curve.

We state here that we do not know any reliable example in the literature where for a

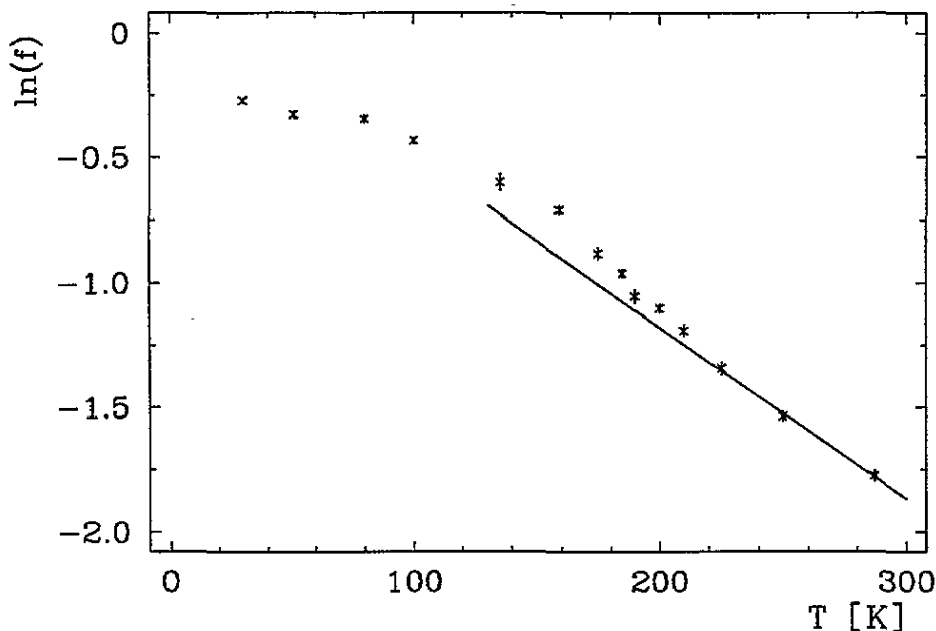


Figure 3. The logarithm of the  $f$ -factor of the crystalline sample b derived from the total area is plotted versus temperature. The straight line is fitted to the high-temperature values.

gradual spin transition the transition curves evaluated by the area fraction of Mössbauer absorption spectra and susceptibility measurements differ by more than the experimental errors. In order to discover such discrepancies one has to make sure that the sample is well crystallized. A metal dilution study will always be helpful, especially the highly diluted case, where only the difference of the molecular  $f$ -factors can give rise to misinterpretation of the area fractions.

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