silicon atoms are five bonds away from each other pair; 2 Hz for the coupling constant is, therefore, quite significant.

The present investigation thus shows that under our photochemical conditions the idea of stabilizing a 1,4-disilabutadiene by the transition-metal carbonyl complex was not realized. In fact, the reaction could be viewed from the other direction. $Mo(CO)_6$ dissociates to a coordinatively unsaturated species, $Mo(CO)_5$, by irradiation which then reacts with 1,2-disilacyclobutene in an oxidative addition process across the Si–Si bond.[10] An attempt to dissociate one more carbonyl ligand from the compound by further irradiation in hope of obtaining a disilabutadiene complex did not work since the title compound seemed to be very stable photochemically.

Acknowledgment. We are grateful to Dr. M. T. Wu of Department of Chemistry, Chun Shan Institute of Science and Technology, for the help of data collection on a Nonius CAD-4F diffractometer. This work has been financially supported in part by the National Science Council, Republic of China.

Registry No. $Mo(CO)_5(C_6H_{10}Si_2F_4)$, 75311-40-9; 3-*tert*-butyl-1,1,2,2-tetrafluoro-1,2-disilacyclobutene, 36091-97-1; $Mo(CO)_6$, 13939-06-5.

Supplementary Material Available: Listings of anisotropic thermal parameters for all nonhydrogen atoms (Table VI) and structure factor amplitudes (Table VII) (15 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4, Canada,
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Electron Spin Resonance and Mössbauer Study of the High-Spin–Low-Spin Transition in $[Fe(phen)_2(NCS)_2]$ and $[Fe(pic)_3]Cl_2 \cdot EtOH$

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Received March 26, 1980

ESR studies have been done on $[Fe^{II}(phen)_2(NCS)_2]$, $[Fe^{II}(pic)_3]Cl_2 \cdot EtOH$ and $[Zn^{II}(pic)_3]Cl_2 \cdot EtOH$ doped with 1 mol % Mn^{2+} (pic = 2-(aminomethyl)pyridine). The spin Hamiltonian parameters D and E were found to decrease steadily with increasing temperature for all three systems, but no change associated with the high-spin–low-spin transition in the iron compounds could be found. Mössbauer studies on the iron compounds showed that the presence of Mn^{2+} had no effect on either the nature of the spin transition or the temperature at which it occurs. The line width of the ESR resonances of Mn^{2+} in $[Fe^{II}(pic)_3]Cl_2 \cdot EtOH$ increases dramatically in the critical region of the spin transition and remains narrow at temperatures above and below the critical region. It is shown that this broadening occurs because the lifetime, τ_{el}, of the spin states of high-spin Fe(II), which is much smaller than 3 ns at higher temperatures, becomes much greater and is in the range 15 $\mu s \gg \tau_{el} \gg$ 3 ns in the critical region.

Introduction

In many transition-metal complexes where the octahedral crystal field (O_h) and the electron pairing energy are comparable, a coexistence of (or a crossover between) the high-spin and low-spin states has been experimentally observed. The transition or crossover can be broadly classified into two types: (1) abrupt or almost discontinuous, as in the case of $[Fe^{II}(phen)_2(NCS)_2]$, or (2) gradual, as in the case of $[Fe^{II}$(2-(aminomethyl)pyridine$)_3]Cl_2 \cdot EtOH$, abbreviated as $[Fe(pic)_3]Cl_2 \cdot EtOH$. Though the crossover in these systems has been studied extensively by various techniques,[1-7] very few studies have been conducted with the aim of probing directly into the mechanism responsible for the spin transition. Specific heat studies[8,9] on $[Fe(phen)_2(NCS)_2]$ and metal dilution studies on the $[Fe_xZn_{1-x}(pic)_3]Cl_2 \cdot EtOH$[7] and $[Fe_xM_{1-x}(phen)_2(NCS)_2]$ (M = Mn, Co, Zn)[6] suggest that the spin transition is cooperative in nature.

ESR studies on paramagnetic impurities such as V^{2+}, Cr^{3+}, Mn^{2+}, etc. have been extensively used to probe ferroelectric phase transitions in many materials.[10-12] In these studies structural changes in the system are detected by changes in the spectra and line width of the resonances of the paramagnetic ion. It occurred to us that a similar study could be done for the Fe(II) spin transition because the ESR spectra of the paramagnetic impurity should be detectable in the paramagnetic phase as well as the diamagnetic phase due to the short electronic relaxation times for the $^5T_{2g}$ state of Fe(II), which will remove most of the dipolar broadening caused by paramagnetic neighbors in the lattice. In the present studies $[Fe(phen)_2(NCS)_2]$ and $[Fe(pic)_3]Cl_2 \cdot EtOH$ were doped with ~1 mol % Mn^{2+}, and the ESR spectrum of Mn^{2+} was measured as a function of temperature. The Mössbauer spectra were obtained for the same samples to establish that the spin transition was not changed by inclusion of the Mn^{2+} ions in the lattice.

Experimental Section

A. Chemical Preparation. KSCN (0.008 mol), $FeCl_2 \cdot 2H_2O$ (0.00396 mol), and $MnCl_2$ (0.00004 mol) were dissolved in dry and freshly distilled ethanol. The precipitated KCl was filtered off and a stoichiometric amount of 1,10-phenanthroline hydrate was added

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(1) G. A. Renovitch and W. A. Baker, Jr., *J. Am. Chem. Soc.*, **89**, 6377 (1967).
(2) E. König and K. Madeja, *Inorg. Chem.*, **6**, 48 (1967).
(3) I. Dézsi, B. Molnár, T. Tarnoczi, and K. Tompa, *J. Inorg. Nucl. Chem.*, **29**, 2486 (1967).
(4) A. T. Casey and F. Isaac, *Aust. J. Chem.*, **20**, 2765 (1967).
(5) W. A. Baker, Jr., and H. M. Bobonich, *Inorg. Chem.*, **3**, 1184 (1964).
(6) P. Ganguli, and P. Gütlich, *J. Phys.* (*Orsay, Fr.*), **41**, C1-313 (1980); submitted for publication in *J. Chem. Soc., Dalton Trans.*
(7) M. Sorai, J. Ensling, and P. Gütlich, *Chem. Phys.*, **18**, 199 (1976).
(8) M. Sorai and S. Seki, *J. Phys. Soc. Jpn.*, **33**, 575 (1972).
(9) M. Sorai, J. Ensling, K. M. Hasselbach, and P. Gütlich, *Chem. Phys.*, **20**, 197 (1977).
(10) K. A. Müller, *Struct. Phase Transitions Soft Modes, Proc. NATO Adv. Study Inst.*, 61 (1971).
(11) W. Windsch and H. Bastauch, *Phys. Status Solidi A*, **16**, K121 (1973).
(12) R. Navalgund and L. C. Gupta, *Phys. Status Solidi B*, **71**, K87 (1975); *Solid State Commun.*, **19**, 1205 (1976); *J. Phys. Soc. Jpn.* **39**, 880 (1975).

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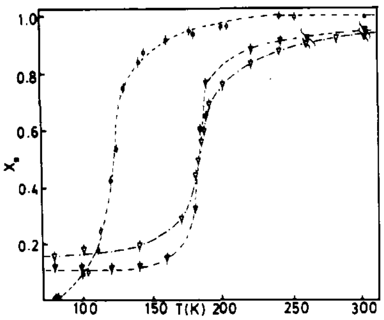

Figure 1. Temperature dependence of the high-spin area fraction (X_H) from the Mössbauer spectra of various samples: ○, $[Fe(pic)_3]Cl_2\cdot EtOH$; ●, $[Fe_{0.99}Mn_{0.01}(pic)_3]Cl_2\cdot EtOH$; ▽, $[Fe(phen)_2(NCS)_2]$ (precipitated); ▼, $[Fe_{0.99}Mn_{0.01}(phen)_2(NCS)_2]$.

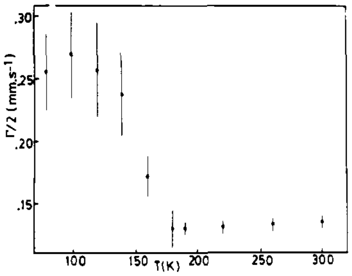

Figure 2. Variation of Mössbauer line width ($\Gamma/2$) of the high-spin species with temperature in $[Fe_{0.99}Mn_{0.01}(phen)_2(NCS)_2]$.

dropwise to the filtrate. In the case of $[Fe_{0.99}Mn_{0.01}(pic)_3]Cl_2\cdot EtOH$, 2-(aminomethyl)pyridine (0.012 mol) was added dropwise to a well-stirred solution of $FeCl_2\cdot 2H_2O$ (0.003 96 mol) and $MnCl_2$ (0.000 04 mol) in ethanol. The precipitated complex was filtered and dried over P_2O_5 in vacuum for several hours. All the preparations were done in dry-nitrogen atmosphere. The purity of the samples was confirmed by elemental analysis and IR spectra.

B. Mössbauer Spectra. The samples were sealed under nitrogen atmosphere in Plexiglas holders. The absorber thickness was about 0.1 mg of $^{57}Fe/cm^2$. The Mössbauer spectra in transmission geometry were recorded by using a Kankeleit type drive[13] in a constant acceleration mode. A 20 mCi $^{57}Co/Rh$ source was kept at 293 K, and the velocity scale was calibrated by using enriched iron foils. The temperature-dependent spectra were recorded by using a standard metal cryostat. Temperatures were measured by using a precalibrated Si diode. The spectra were fitted to Lorentzians by using iterative procedures.

C. ESR Spectra. The samples were sealed under vacuum in quartz tubes. ESR spectra were recorded by an X-band Varian E-12 spectrometer. A gas-flow cryostat was used to control the temperature, and a copper–constantan thermocouple was used to measure the temperature.

Results

A. Mössbauer Spectra. The Mössbauer spectra of both compounds show two quadrupole split doublets characteristic of the high- and low-spin species in the lattice. The temperature dependence of the high-spin fraction obtained from the spectra are plotted in Figure 1. The transition characteristics of the pure and the 1 mol % Mn^{2+} doped $[Fe(pic)_3]Cl_2\cdot EtOH$ complex are identical. For $[Fe_{0.99}Mn_{0.01}(pic)_3]Cl_2\cdot EtOH$ the transition is gradual and there is complete conversion to the low-spin state at lower temperatures. The transition characteristics of $[Fe(phen)_2(NCS)_2]$ depends remarkably on the preparation. The transition becomes sharp depending on the crystalline state of the compound.[6] In the case of $[Fe_{0.99}Mn_{0.01}(phen)_2(NCS)_2]$ the transition is sharp, but about 12 mol % of the iron remains in the high-spin state

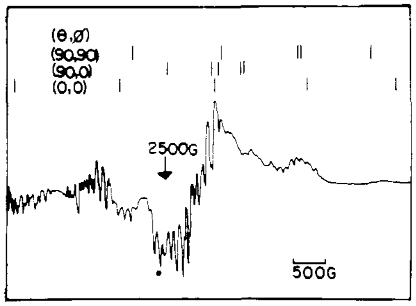

Figure 3. ESR spectrum of $[Fe_{0.99}Mn_{0.01}(pic)_3]Cl_2\cdot EtOH$ at 86 K. The "turning points" used in estimating D and E are indicated by lines. The asterisk indicates the line whose width was followed as a function of temperature.

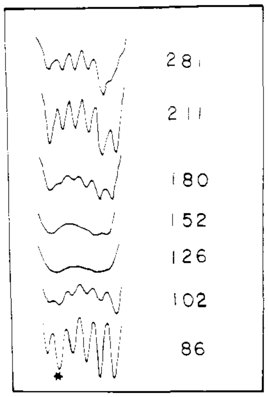

Figure 4. Portion of ESR spectrum at various temperatures for $[Fe_{0.99}Mn_{0.01}(pic)_3]Cl_2\cdot EtOH$. The transition whose width was measured as a function of temperature is indicated by an asterisk.

below the transition temperature. The transition temperature, however, is the same as in the undoped compound.

The line width of the Mössbauer spectral lines from the high-spin iron in $[Fe_{0.99}Mn_{0.01}(phen)_2(NCS)_2]$ is shown as a function of temperature in Figure 2. This appears to show a transition at temperatures somewhat lower than displayed in Figure 1, but this is due to the fact that, when an observed line is the sum of a broad and a narrow line, the average line width is primarily determined by the species giving rise to the narrow line at relatively low concentrations. We have been able to quantitatively explain the line-width behavior with a model that assumes the 12 mol % of Fe(II) ions that remain in the high-spin state at all temperatures always exhibit the broad line while the 88 mol % of Fe(II) ions that participate in the low-spin–high-spin transition exhibit the narrow line width in the high-spin state. It could be that the 12 mol % also change line width at higher temperatures, but we have no way of confirming this. It is, however, true that the residual high-spin Fe(II) often found at low temperatures in $[Fe(phen)_2(NCS)_2]$ is in a different physical environment at low temperatures than the high-spin Fe(II) observed after the transition. A recent report[14] on the effect of grinding on the high-spin–low-spin transition in the Fe(III) complexes would suggest that this residual high-spin Fe(II) is located at the surface of crystallites or near crystal imperfections of some sort. This would explain the broader lines.

B. ESR Spectra. The spectra are typical powder spectra for an $S = {}^5/_2$, $I = {}^5/_2$ system with zero field interaction less than the Zeeman interaction. Figure 3 shows the spectrum of $[Fe_{0.99}Mn_{0.01}(pic)_3]Cl_2\cdot EtOH$ at 86 K. The line widths here are narrow enough to give well-resolved hyperfine patterns. The line widths change dramatically as the temperature is

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[13] E. Kankeleit in "Mössbauer Effect Methodology", Vol. 1, I. J. Gruverman, Ed., Plenum Press, New York, 1965, p 47.

[14] M. S. Haddad, W. D. Federa, M. W. Lynch, and D. N. Hendrickson, *J. Am. Chem. Soc.*, **102**, 1468 (1980).

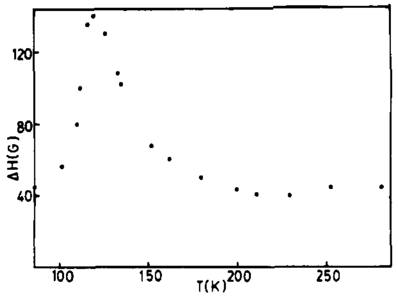

Figure 5. Variation of ESR line width (ΔH) in $[Fe_{0.99}Mn_{0.01}(pic)_3]Cl_2 \cdot EtOH$ as a function of temperature.

increased. Figure 4 shows the region of the spectrum containing the (M_S, M_I) $\leftrightarrow$ ($M_S - 1$, M_I) transition at various temperatures where $M_S = {}^1/_2$ and $M_I = {}^3/_2$ and ($\theta = 90°$, $\phi = 0°$) for the field direction. The indicated transition is designated by an asterisk in Figures 3 and 4, and the line width of this transition as a function of temperature is plotted in Figure 5. The maximum line width is at 121 K which is the transition temperature T_c found from Mössbauer spectra for the spin transition. The Mn^{2+} ESR spectra for $[Fe_{0.99}Mn_{0.01}(phen)_2(NCS)_2]$ are much broader at all temperatures, making it almost impossible to resolve any hyperfine patterns. It is apparent from the spectra that the lines do broaden also in the vicinity of the transition temperature of 182 K, but no reliable measure of line widths was possible in this system.

It was assumed that the Mn^{2+} spectra could be fitted to a spin Hamiltonian of the form

$$\mathcal{H} = g\mu_e \mathbf{S} \cdot \mathbf{B} + D[S_z^2 - {}^1\!/_3 S(S+1)] + E(S_x^2 - S_y^2) + \mathcal{A}\mathbf{S} \cdot \mathbf{I} \quad (1)$$

We first tried calculating a powder pattern for assumed values of the parameters g, D, E, and $\mathcal{A}$ and comparing this with the experimental spectra. However, this had to be abandoned for two reasons. (1) The rapid variation with orientation of many transitions made it necessary to calculate all lines and their intensities for every 1° of both polar angles θ and ϕ, resulting in a calculation which consumed too much time on our computer if we wished to calculate the spectrum over the range $0 < B > 0.7$ T. (2) Our Calculation used perturbation equations to third order, and it became apparent that D was large enough to require an exact solution of eq 1. We, therefore, resorted to obtaining less accurate values of D and E by locating the prominent "turning points" in the powder spectra and identifying these with the spectra for the three principal axes of the system where (θ, ϕ) = (0°, 0°), (90°, 0°), and (90°, 90°). The fitted "turning points" are indicated in Figure 3. In a near axial spectrum the most prominent "turning points" will be (90°, 0°) and (90°, 90°). Exact solutions of eq 1 (without the $\mathcal{A}\mathbf{S} \cdot \mathbf{I}$ term) were obtained for values of B from 0 to 0.7 T and allowed transitions identified for which ΔE equals the photon energy of our spectrometer. The field positions for the nonzero transitions for the three principal axes were matched with the centers of hyperfine sextets observed in the experimental spectra, and D and E varied to get a good fit. Although this method will lead to systematic errors in determining D and E, it is suitable for our purposes since we are primarily interested in any changes in D and E with temperature rather than the accurate determination of D and E at any given temperature. In fact, a simple plot of a prominent feature in the spectrum vs. temperature would serve to establish the existence of a change in D and E in the transition region. Plots of D and E vs. temperature for $[Fe_{0.99}Mn_{0.01}(phen)_2(NCS)_2]$, $[Fe_{0.99}Mn_{0.01}(pic)_3]Cl_2 \cdot EtOH$, and $[Zn_{0.99}Mn_{0.01}(pic)_3]Cl_2 \cdot EtOH$ are given in Figures 6–8.

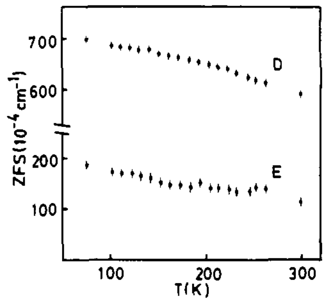

Figure 6. Temperature dependence of the zero field splitting (ZFS) parameters D and E in $[Fe_{0.99}Mn_{0.01}(phen)_2(NCS)_2]$.

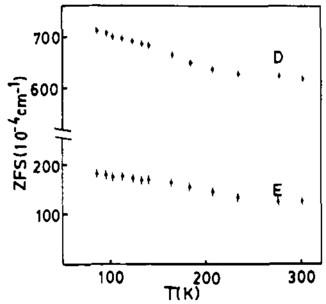

Figure 7. Temperature dependence of the zero field splitting (ZFS) parameters D and E in $[Fe_{0.99}Mn_{0.01}(pic)_3]Cl_2 \cdot EtOH$.

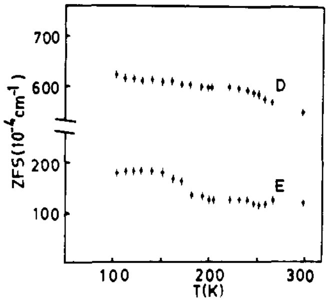

Figure 8. Temperature dependence of the zero field splitting (ZFS) parameters D and E in $[Zn_{0.99}Mn_{0.01}(pic)_3]Cl_2 \cdot EtOH$.

Discussions

The Mössbauer results show that the Mn^{2+} impurity does not affect the nature of the transition or the temperature, T_c, at which it occurs. The ESR line-width changes demonstrate that the spin transition occurs in Fe(II) ions adjacent to the Mn^{2+} ion at the same temperature as for the Fe(II) ions in the bulk lattice. Thus the appearance of the Mn^{2+} ions do not disturb in any appreciable manner the transition we are trying to study.

It is clear from Figures 6 and 7 that no change in either D or E occurs in the range of the high-spin–low-spin transition. The curves for $[Zn_{0.99}Mn_{0.01}(pic)_3]Cl_2 \cdot EtOH$ in Figure 8 further show that the observed temperature dependence is just that found in systems that do not undergo a spin transition. Thus it appears that any structural changes that occur during the spin transition are short-range ones inside the Fe(II) complex and not long-range ones involving the total lattice.

Line-width broadening of magnetic resonance lines in a phase transition are not unknown. Broadening of ESR lines during a ferroelectric phase transition has been observed[15,16] and attributed to the fact that during the transition various

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(15) K. A. Müller and Th. von. Waldkirch, "Local Properties at Phase Transitions", K. A. Müller and A. Rigamonti, Eds., North-Holland Publishing Co., Amsterdam, 1976, p 187.

(16) R. R. Navalgund and L. C. Gupta, *Phys. Status Solidi B*, **71**, K87 (1975).

sites in the crystal experience a range of D and E values. Such an explanation can be ruled out in the case of the broadening of resonances for $[Fe_{0.99}Mn_{0.01}(pic)_3]Cl_2 \cdot EtOH$ because no change in D or E occurs in the spin transition.

The broadening is likely due to local magnetic fields generated by the paramagnetic ions. The magnitude of these fields depends on the correlation time or lifetime of a given spin state of the Fe(II) ion. When the lifetime is long, the magnetic fields are of the order of $\sim\mu R^{-3}$, where μ is the magnetic moment and R the distance between Mn^{2+} and Fe(II). When $\mu = 5.5\ \mu_B$ and $R = 7$ Å, the magnetic field is ~ 140 G. If the lifetime of an M_S spin state for the $S = 2$ state of Fe(II) is much shorter than the inverse line width caused by dipolar broadening, then the local fields experienced by the resonant spin are much smaller due to an averaging over all spin states of the paramagnetic ion and have a magnitude of the order of $\sim\chi B_0 R^{-3} = (\mu^2/3kT)B_0R^{-3}$. This gives ~ 0.4 G for $\mu = 5.5\ \mu_B$, $R = 7$ Å, $T = 121$ K, and $B_0 = 3000$ G.

Clearly the broadening can be explained by assuming the lifetime of an Fe(II) spin state is long in the critical-temperature region relative to the inverse line width which for 100-G line widths means the time is much greater than 3×10^{-9} s. An upper limit can be put on this lifetime by line widths observed in proton NMR studies of both complexes[3,17] which exhibit line-width changes 1 order of magnitude smaller (in G). Since R is considerably smaller for the proton than for the Mn^{2+} ion, this means that for proton NMR we are in the line-narrowing limit in which the spin lifetime of Fe(II) is much smaller than the inverse line width. This makes the lifetime much less than 1.5×10^{-5} s. It should be emphasized here that the lifetimes we are discussing are that of individual M_S states in the high-spin $S = 2$ state of Fe(II). The lifetime of the high-spin state ($S = 2$) or low-spin state ($S = 0$) is $\gtrsim 10^{-7}$ s as determined by our observation of separate doublets for both states in the Mössbauer spectra (the nuclear lifetime of the 14.4-keV state of ^{57}Fe is $\sim 10^{-7}$ s).

The fact that for NMR we are in the line-narrowing limit is confirmed by plotting the line width vs. T^{-1} and finding a straight-line dependence at temperatures well above the transition temperature. A similar plot for the ESR data does not yield a straight line as the line width falls off much too rapidly with increasing temperature.

Having established that there is a rapid increase in the lifetime of a spin state in the critical region, it is interesting to note that the maximum broadening occurs almost exactly at T_c, the temperature when equal fractions of high- and low-spin states are present. In fact we find that the line width is almost a linear function of $X_{LS}X_{HS}$, where X_{LS} and X_{HS} are area fractions of low- and high-spin iron (as determined from the Mössbauer resonances). A similar increase in spin-state lifetimes in the critical region has been observed[18] by NMR studies on antiferromagnetic systems and is apparently predicted by present theories[19] of phase transitions.

Several theories for the high-spin–low-spin transition have been advanced. Slichter and Drickamer[20] and Zimmerman and König[21] have advanced similar theories which assume a statistical distribution throughout the sample of high- and low-spin iron molecules. An interaction parameter was included to make the energy of one iron molecule dependent on the spin of its nearest neighbors. The mechanism for this interaction was not specified. Gütlich et al.[22] have extended a suggestion by Sorai and Seki[23] to give a phenomenological theory which assumes domains of high and low spin rather than a statistical distribution. The domains in $[Fe(phen)_2(NCS)_2]$ were estimated to contain ~ 90 molecules and in $[Fe(pic)_3]Cl_2 \cdot EtOH$ ~ 3.5 molecules. They suggested that the cooperative coupling occurred through a spin–phonon interaction.

Our study cannot choose between these theories. If the domains were large, we might expect to see in the transition region a spectrum which is a sum of the spectra for Mn^{2+} in the two different phases. However, in the case of $[Fe(phen)_2(NCS)_2]$ where the domains are supposed to be large, the line widths were too large in both the diamagnetic and paramagnetic phases to look for such an effect. In the case of $[Fe(pic)_3]Cl_2 \cdot EtOH$ the domain size was too small to make any difference. The only thing that we have shown here is that the spin transition is not driven by a structural phase change.

Conclusions

We have established that no large changes occur in the lattices of $[Fe(phen)_2(NCS)_2]$ and $[Fe(pic)_3]Cl_2 \cdot EtOH$ during the high-spin–low-spin transition. For $[Fe(pic)_3]Cl_2 \cdot EtOH$ we have found that the lifetime, τ_{el}, of a given spin state of the high-spin form of Fe(II) is in the interval $1.5 \times 10^{-5}\ \text{s} \gg \tau_{el} \gg 3 \times 10^{-9}$ s in the critical region but becomes much smaller than 3×10^{-9} s at higher temperatures. Further we have established that the residual Fe(II), which does not undergo a spin transition, that is often found in samples of $[Fe(phen)_2(NCS)_2]$ is in a different physical environment from that of the Fe(II) that exhibits such a transition.

Acknowledgment. This work was supported by the National Science and Engineering Research Council of Canada, The Deutsche Forschungsgemeinschaft, and NATO Research Grant No. 1372. The authors gratefully acknowledge the financial help. P.G. thanks the Alexander Von Humboldt Foundation for the award of a fellowship from July 1977 to Sept 1979.

Registry No. $Fe^{II}(phen)_2(NCS)_2$, 14692-67-2; $[Fe^{II}(pic)_3]Cl_2$, 18433-69-7; $[Zn^{II}(pic)_3]Cl_2$, 61919-63-9; Mn, 7439-96-5.

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(17) P. Ganguli, P. S. Rao, and B. R. McGarvey, submitted for publication.

(18) P. Heller, "Local Properties at Phase Transitions", K. A. Müller and A. Rigamonti, Eds., North-Holland Publishing Co., Amsterdam, 1976, p 447.

(19) H. Thomas, "Local Properties at Phase Transitions", K. A. Müller and A. Rigamonti, Eds., North-Holland Publishing Co., Amsterdam, 1976, p 3.

(20) C. P. Slichter and H. G. Drickamer, *J. Chem. Phys.*, **56**, 2142 (1972).

(21) R. Zimmerman and E. König, *J. Phys. Chem. Solids*, **38**, 779 (1977).

(22) P. Gütlich, H. Köppen, R. Link, and H. G. Steinhäuser, *J. Chem. Phys.*, **70**, 3977 (1979).

(23) M. Sorai and S. Seki, *J. Phys. Soc. Jpn.*, **33**, 575 (1972); *J. Phys. Chem. Solids*, **35**, 555 (1974).