Inorganica Chimica Acta, 72 (1983) 269–275

The Hierarchic Order in the Solid State.
Part III. Spin Transitions in Certain Iron Complexes*

V. GUTMANN and G. RESCH

Institute of Inorganic Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria

Received October 10, 1982

In the course of spin transitions a singular 'state' of greatest inner dynamics is passed: it denotes the LS:HS ratio, at which both the specific heat and the change in entropy have maximum values, and at which the system's properties are virtually independent from its history and its defect structure. This 'state' is considered as that of highest dynamic order (HDO). Suggestions are made for the characterization of the hierarchic order of a given system by relating properties to those exhibited in the state of HDO. The concept of the hierarchic order also offers an explanation both for the residual paramagnetism at very low temperatures and for the hysteresis phenomena [1, 2].

Introduction

So-called 'anomalies' or 'curiosities' have been reported for spin cross-over complexes of compositions $Fe(phen)_2(CNX)_2$, where X = S or Se [3, 4], and $[Fe(X\text{-}SalEen)_2]Y$, where X-SalEen results from the Schiff base condensation of X-substituted salicylaldehyde and N-ethylethylenediamine [5, 6]. These are

(i) the variation of the effective magnetic moments per metal ion *vs.* temperature which does not correspond to a Boltzmann distribution over the thermally populated high spin and low spin states [5];

(ii) the residual paramagnetism at very low temperatures [3];

(iii) the gradual and incomplete LS → HS transitions [3];

(iv) the influence on the transition by the mode of preparation [7–10], the nature of ligands [11–17], the presence of other metal ions [4, 6, 18], and the actions of grinding [4] and of pressure [19–22]. The possibility that grinding might lead to compound decomposition or to introduction of impurities, and that either or both might help to explain the observations, has been eliminated: a ground sample was dissolved in methanol and the solution evaporated to dryness to give a solid which would retain any impurities introduced by its previous treatment. However, the properties were the same as those found for the unperturbed material;

(v) the time dependence of magnetic susceptibilities [9];

(vi) the hysteresis effects [4, 6, 23, 24].

In the following account no attempt will be made to put the experimental facts entirely on theoretical grounds. Instead we may try to consider all evidence and to relate this to the system's properties. In this way it is hoped to obtain at least some information from the statistical data, to learn some of the dynamic relationships which are not directly observable, and to try to obtain indirect knowledge about the hierarchic order.

The 'State' of Highest Dynamic Order

In order to characterize a transition, the so-called transition temperature T_c is used [3]. This is defined as the temperature of equal amounts of co-existing spin states. However, the spin states are not equienergetic at this point, and it is not true that the HS-species is more favoured above and the LS-species more favoured below T_c, which is known to depend on the 'history' of the sample. A more realistic point of reference for a system of given analytical composition should represent the 'state' which is most significant for the transition in the system under consideration. This cannot be 'chosen', but must be found by experiment.

It is known that in the course of phase transitions high values for heat capacities are reached [25]. Indeed, Sorai and Seki [26, 27] found similar effects

---

*Extended version of a paper presented at the XXII International Conference on Coordination Chemistry in Budapest, August 23, 1982.

0020-1693/83/$3.00

for crystals of $Fe(phen)_2(NCS)_2$ and $Fe(phen)_2(NCSe)_2$. For each complex they noted an enormous peak in the heat capacity *vs.* temperature curve and a 'jump' of the extrapolated 'normal' heat capacities ascribed to the LS- and HS-species respectively. For $Fe(phen)_2(NCS)_2$ the heat capacity rises from 657 J K^{-1} mol^{-1} at 174.9 K more than ten times to 7164 J K^{-1} mol^{-1} at 176.3 K, and drops to 437 J K^{-1} mol^{-1} at 180.5 K. The peak of c_p = 8011 J K^{-1} mol^{-1} is found at 231.3 K for $Fe(phen)_2(NCSe)_2$. The same authors [26, 27] found further that the values for ΔS are much greater in the course of the transition than expected only for the magnetic entropy change and that the change in ΔS is greatest at the temperature of greatest specific heat. Under these conditions the system appears to have reached the greatest inner dynamics and the greatest 'differentiation'.

At the 'state' of greatest dynamics any change in energy leads to a less differentiated and more rigid system. This singular 'state' seems both to separate and to connect the more rigid 'structures', and hence to represent the 'turning point' in the course of the transition. It must be emphasized, however, that this 'state' cannot be characterized precisely by a temperature. The temperature at which this state is reached may vary according to the 'history' of the sample, to the environmental conditions (chemical environment, actions of pressure, mechanical forces, fields, irradiation), and even according to the direction in which the transformation takes places. For example, both the temperature of highest heat capacity and the numerical value of the latter will be different on heating and on cooling the same sample [4, 24] (hysteresis effect, section 4). Thus, the dynamic properties of an object will depend on the conditions under which they are studied, and the dynamic order cannot be characterized for an object as such without consideration of all boundary conditions.

The authors believe that the critical LS:HS ratio for the rearrangement may be least sensitive toward such boundary conditions. The critical LS:HS ratio as characterized by highest c_p and ΔS values may be obtained by considering the μ_{eff}/Fe *vs.* temperature plot for the same sample under consideration. So far results must be consulted which have been found for different samples.

In the μ_{eff}/Fe *vs.* temperature plot the LS:HS ratio characteristic for the rearrangement seems to be represented by the point of inflexion of the transition curve. This point remains less accurate the sharper the transition. The inspection of such plots indicates, however, that the LS → HS transition curves for samples of the same analytical composition, but of different origin and pretreatment show a point of intersection*. For example, the LS → HS transition curves of $Fe(phen)_2(NCS)_2$ complexes are different for the sample precipitated from methanol solutions, for that obtained by extracting a phenanthroline group from $Fe(phen)_3(NCS)_2 \cdot H_2O$ by acetone [10], and for a ball-milled sample [23]. The transition curves of these samples are found to intersect at μ = 4.95 and at 176 K. This is also the temperature of greatest entropy change, and hence of greatest differentiation and greatest inner dynamics. Likewise, a point of intersection* is found in the μ_{eff}/Fe *vs.* temperature plots for the LS → HS transitions of samples of composition $[Fe(X\text{-}SalEen)_2]Y$, which have been ground in different ways: chromium-doped [6] or subjected to pressure (Fig. 1).

It is well known that mechanical treatment of a sample of given composition produces alterations in the so-called 'defect-structure'. Thus, different transition behaviour of samples of different pretreatment may be related to differences in defect-structure, and these have been considered to be related to differences in hierarchic organization [1, 2]. This singularity of the point of intersection* in the μ_{eff}/Fe *vs.* temperature plot is the independence of the properties of the samples under consideration from their respective defect structures. At this point a 'state' is produced in which the properties cannot be related to observable static aspects of structure. The properties appear to be determined by the more or less well-developed dynamic aspects, which are not directly observable. This state of greatest inner dynamics is at the same time a point of 'inner rest' for the system, which is dynamically maintained, and hence the system has greatest flexibility. This 'state' may therefore be considered as the 'state' of highest dynamic order (HDO). Only in this 'state' is the equilibrium fully defined by analytical composition and the variables of state, as independent from pretreatment and defect structure. This means that ΔH for the transition and $T\Delta S$ have attained the same numerical values (compensation effect), and also that only at this point is the entropy independent from the static aspects of structure to which entropy is frequently considered as related.

It has been emphasized that the static structural aspects of order must be dynamically maintained [1, 2]. Evans [28] has found that by irradiating molybdenum, voids (SMM-centres) may form into three-dimensional arrays to provide a body-centered cubic 'superlattice' structure with the same crystallographic axes as those in the molybdenum structure. The voids are continuously changing positions within the crystal lattice, and hence the static aspects of the 'void lattice structure' represent time and space

---

*In a strict sense a sharp point of intersection would be an idealization.

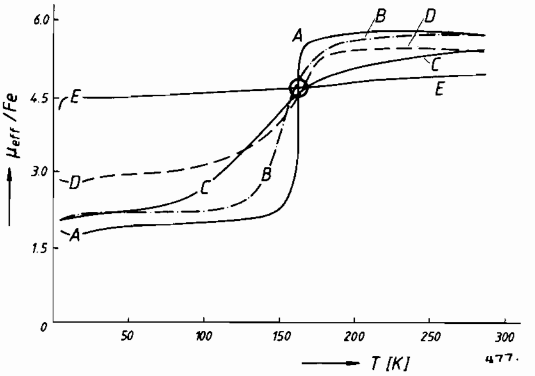

Fig. 1. The point of intersection in the μ_{eff}/Fe *vs.* temperature plot for $[Fe(3\cdot OCH_3\text{-}SalEen)_2]PF_6$; A, unperturbed; B, subjected to pressure; C, unperturbed microcrystalline 50% Cr-doped material; D, sample A after grinding in a ball-mill; E, sample C after grinding in a ball-mill.

averages of the actual positions of the voids. These appear to provide a mobile matrix by which the static aspects of the crystal structure are dynamically maintained. An illustration for these facts has recently been given by means of a so-called Rubik-cube [29].

The enormous role of the dynamic aspects of order for the understanding of the properties of a solid is most accentuated at the state of HDO. The dynamic aspects of order are not directly observable, but their regularities under different conditions may be found, and it must be considered [1, 2] that

(i) any system is microscopically differentiated,

(ii) the different parts are subject to ordered motions, and

(iii) the different parts are subordinated to each other, as is characteristic for a so-called hierarchic order [1, 2].

Transition Properties and 'Defect Structure'

Before discussing, the ways by which the hierarchic order of a given spin cross-over sample may be characterized, we may consider the properties in states apart from that of HDO, *i.e.* in states where the properties appear related to static aspects of order. In these the changes in observable properties appear related to structural changes, and we may try to understand the residual paramagnetism and the hysteresis effects.

The structural differences between LS- and HS-species are in agreement with the bond length variation rules [30]: in the $Fe(phen)_2(NCS)_2$ complexes the metal–NCS distances are shorter and the Fe–N(phen) distances longer in the HS- than in the LS-species [3]. The FeN_6 chromophore is somewhat more distorted in the HS-than in the LS-species [3] (the situation is different for transitions in systems where the coordination numbers are changed and the molecular geometries more strongly affected than in the complexes under consideration [31–33]. Below the point of highest dynamic order, HS-units appear to be under strain of the LS-network which exerts resistance against lattice expansion, and this is greater the less developed the defect structure. The more developed the defect structure, the more gradual becomes the transition. The defect structure is known to become more developed by the actions of grinding, doping, pressure, fields or irradiation [1, 2]. The said actions may lead to changes in surface area and to increasing dislocation- and point defect-densities associated with increasing mobilities within the system. The crystallographic and various spectroscopic properties are hardly changed, but the results of magnetic and Mössbauer measurements reveal different amounts of LS- and HS-species. Their local distributions within the system at any given temperature seem to be related to the matrix of the defect pattern: as HS-units are in states of higher energy than LS-units, their formation may take place preferentially at the sites of high local energies, *i.e.* in building units serving high hierarchic levels [9]. As the parts are differentiated and subordinated, the conditions for the Boltzmann distribution over the thermally populated high spin and low spin states are no longer precisely fulfilled.

At a given low temperature the number of units in the highest states of energy (*i.e.* those serving the highest levels) is small, but never zero, and it is greater in ground crystals than in 'well-developed' crystals. The occupancies of positions in the highest hierarchic levels (*i.e.* the craters [2]) by HS-units, even at very low temperatures, seem to account for the residual paramagnetism which is accordingly greater in a ground than in a well-developed crystalline material. As the temperature is increased, positions at the flat surface areas and at dislocation nodes may gain sufficient energy, in order to allow the formation of HS-units. Further increases in temperature may lead to the formation of HS-species along the dislocation lines and then at point-defects (SMM-centres). The distribution of HS-units at low temperatures may be illustrated by means of an energy density map, as shown both for a well-developed crystal (Fig. 2a) and for a ground material (Fig. 2b). In the former the few sites of higher energy are soon occupied by HS-units, which appear somewhat 'separated' by the large and compact domains of LS-species. These are hardly differentiated and provide a rather rigid framework, in which all building units become subject to increasingly constrained conditions as the temperature is increased. This is because (i) the HS-units cannot take up much more energy, (ii) no preferred sites for their formation are available, and (iii) the flexibility of the lattice is low and its resistance to lattice expansion, as involved in the conversion, is great. The 'rigid' LS-domains collapse

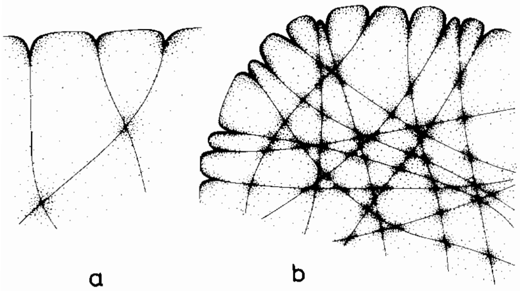

Fig. 2. Illustration of the energy differentiation within crystals. The dark spots indicate point defects and the dark areas regions of highest energy per part; (a), reasonably pure crystal, grown from a melt or from a solution; (b), after grinding.

as soon as most of the building units have gained sufficient energy for the transformation. The system passes very rapidly through the state of highest dynamics and again reaches quickly a rather rigid state of low differentiation.

In a ground material (Fig. 2b) the LS-domains are 'penetrated' more strongly and dominated to a greater extent by a great number of sites of higher energies, at which conversion into the HS-species takes place more readily. They are mobile and dominate other lattice areas. The whole lattice is more flexible, and less resistance is provided against gradual changes (the transition is more gradual). A greater lattice flexibility is maintained after the point of HDO has been passed, and the amount of LS-species will be greater accordingly. The more developed the defect structure and the differentiation (as produced for example by grinding) the more are the parts subordinated to each other, the greater is the amount of energy which can be stored in the HS-parts, and the more are the remaining LS-parts prevented from gaining energy as the temperature is raised.

The action of pressure involves also mechanical deformations. Interactions between grain boundaries due to the action of pressure are known to lead to the formation of additional necks and craters [34], which are hierarchically higher than flat and less 'perturbed' surface areas [2]. The surface becomes more differentiated, and the dislocation density and the point defect density may be increased by several orders of magnitude [35]. The greater differentiation of the whole system is also indicated by line-broadening in the X-ray pattern [36, 37], and in an increase in HS-content below and in an increase of LS-content above the state of HDO, as compared to the same material under normal pressure. Likewise, certain doping effects may lead to greater differentiation and increased dynamic order: in the course of the dissolution process solute particles (SMM-centres) will gain energy even from the lowest hierarchic level, so that the system becomes more differentiated.

Memory Effects and Phenomena

Hysteresis effects are reflected in the μ_{eff}/Fe *vs.* temperature curves: as the defect structure is more developed at low LS-content (at low temperature), LS → HS conversion is favoured and it is opposed at high HS-content (at higher temperature). As for the LS → HS conversion, energy is required and the following assumption may be made with regard to the energy redistribution within the system by increase in temperature: at low LS-content (and at low temperature) most of the energy gained by the system is distributed over the units in the lowest hierarchic level, and only a small fraction is retained by the units in the highest levels. The situation is different at high HS-content, when more energy is retained by the units serving the higher levels. Both effects are greater the more developed the defect structure.

Such conclusions were also drawn from the results of thermally stimulated luminescence phenomena of metals. When a system is cooled, the parts in the higher levels retain energy more strongly than those in the lower levels, and when a system is heated, energy is less rapidly stored by the parts in the higher levels than by those in the lower levels [38]. Thus, the more strongly pronounced inertia of the higher level toward changes seems to be decisive for the so-called 'memory effects' and hysteresis phenomena. In this way explanations are provided for the time-dependent decrease of the magnetic moment by annealing $[Fe(II)L_2](BF_4)_2$ (L = phen or bpy) [39], for the retention of the HS-species after rapid cooling [40], for the different data which have been obtained in heating and in cooling modes for $Fe(phen)_2(NCS)_2$ [4, 23], and for the well pronounced hysteresis effects observed for the HS → LS conversion in solid $[Fe(phy)_2](ClO_4)_2$ where phy = 1,10-phenanthroline-2-carbaldehyde phenylhydrazone [39]. For a sample which is gradually cooled from high temperatures, the said conversion takes place at a lower temperature than that for a sample which is gradually heated from low temperature. The different behaviour on heating (LS → HS conversion) and on cooling (HS → LS conversion) [23] is further influenced by the 'history' of the sample. For example, grinding is expected to lead to

(i) more pronounced hysteresis effects, *i.e.* greater differences of the transition curves on heating and cooling modes [23],

(ii) lowering of the maximum values of the heat capacities,

(iii) broadening of the temperature ranges of higher c_p-values,

(iv) higher c_p-values on cooling than on heating a given sample, the differences being greater as the sample has been ground more thoroughly.

This means that

(i) the hierarchic order is smaller the higher and the sharper the peak in the heat capacity *vs.* temperature plot. (For an ideal system it should be infinitely high (Fig. 3).

(ii) the hierarchic order is greater the lower and broader the range of higher c_p in the heat capacity *vs.* temperature curve (Fig. 3);

(iii) on cooling the sample, part of the greater dynamics at high temperature is retained [38], and

(iv) on heating the sample, part of the lower dynamics at low temperature is retained;

(v) the effects are greater the higher the structural and energetic differentiation of the sample [38, 41].

Suggestions for the Characterization of the Hierarchic Order

Hierarchic order is found in any given system as a basic requirement for an existing body in its dynamic interactions with its environment [2]. The hierarchic order is shaped by the requirements for the existence of the real body (differentiation) and by the dynamically maintained interactions with environment [2]. It appears impossible to obtain sufficient evidence even for the static aspects of differentiation (for example from electron microscopic observations) under all possible conditions. It may be possible, however, to compare different states in hierarchic order for a material of given analytical composition. For this purpose a suitable point of reference must be found.

In order to compare the hierarchic order between systems of the same analytical composition and of different origin, pretreatment or environmental conditions, the state of highest hierarchic order should be the most suitable state. Because the properties at this state are independent from the defect structure, it is impossible to account for the actual hierarchic order as such in this 'state': the properties are dominated by the unobservable dynamic aspects of order and seem unrelated to the observable static aspects of order. The situation is similar to that for the standard hydrogen electrode which is used as a reference system, although its single electrode potential is unmeasurable. The following possibilities may be considered:

1. The heat capacity of a system is related to its inner dynamic features, as they are established through its hierarchic order. Aspects of the latter within a real solid material capable of undergoing a phase transition (in the present case a LS → HS transition) may be seen from the heat capacity *vs.* temperature plot: at the LS:HS ratio which corresponds to the state of HDO of the real system, a peak is found (Fig. 3).

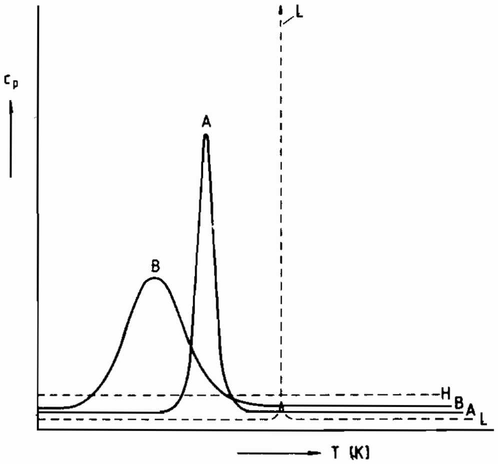

Fig. 3. Illustration of specific heat *vs.* temperature curves for real samples of the same analytical composition, differing in hierarchic order, and for idealized systems. A has a lower hierarchic order than B. H refers to the idealization of highest and L to that of lowest hierarchic order.

Only for a hypothetical system of highest possible dynamic order would no peak be found (Fig. 3H), because in this system the LS:HS ratio corresponding to the state of HDO would be maintained over a wide temperature range. In other words the dynamic features which are best developed at the state of HDO are 'spread' over a wide range of temperatures, and the greater flexibility of the system over the latter would be reflected in somewhat higher c_p-values (Fig. 3H) than they are found for real systems at any temperature outside the transition range of the real system (Fig. 3, curves A and B). The system would be extremely flexible.

The lower the dynamic order, the more rigid and less flexible will be the LS- and HS- structures respectively, and the c_p-values will be smaller at temperatures outside the transition range (Fig. 3, curves A and B). However, the peak in the heat capacity *vs.* temperature plot will be higher, and the temperature range of high heat capacity more narrow, the lower the actual dynamic order of the system: the more will the rigid 'phases' be 'separated' from each other by a narrow temperature region, in which the dynamic order is much higher. This appears to be expressed by a 'barrier' of high c_p-values, because more dynamic changes will be required for the transformation. In Fig. 3 the hierarchic order of sample B is higher than that of sample A. For an 'ideal' system of lowest dynamic order possible the lowest c_p-values would be expected over the wide range of temperatures, except the temperature of maximum c_p-value which would be infinitely high (Fig. 3L), and no transition would be possible. Both the broadness of the peak in the heat capacity *vs.* temperature plot and the maximum value for the heat capacity may be used as indications of the hierarchic order for the system under consideration (Fig. 3).

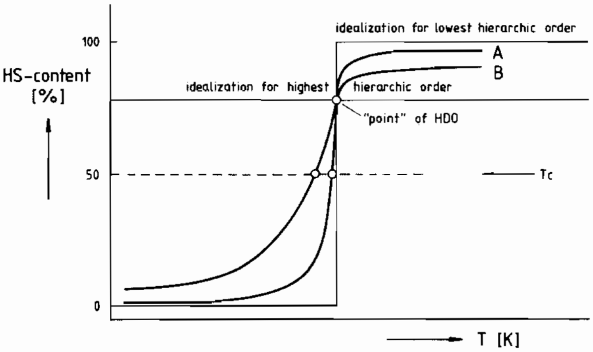

Fig. 4. Illustration of transition curves for real samples of the same analytical composition differing in hierarchic order, and for idealized systems. The slope of the curve at the point of intersection (corresponding to the state of HDO) may be considered as indicating the hierarchic order of the given sample. A has a lower hierarchic order than B.

2. The μ_{eff}/Fe *vs.* temperature curves may also provide indications for the hierarchic order [41]. For a system of lowest hierarchic order possible, the LS → HS transition would take place abruptly, and T_c would be identical with the temperature of HDO (Fig. 4). On the other hand, for an idealized system of highest possible hierarchic order the LS:HS ratio characteristic for the HDO should remain constant over a wide temperature range (Fig. 4). The combined actions of chromium-doping and ball-milling $[Fe(3OCH_3\text{-}SalEen)_2]PF_6$ lead to a material which comes close to this idealization [4] (Fig. 1E). The system has the remarkable ability to distribute the changes in energy over the various hierarchic levels in such ways that its dynamic properties are nearly maintained. Increase in temperature does not lead to further HS-formation, because the HS-domains take up most of the additional energy and the energies within the LS-domains remain less affected. Decrease in temperature does not produce further LS-units, because the LS-domains are further stabilized by loosing energy whereas the HS-species remain stable by retaining energy as required for their co-existence within the highly differentiated and highly flexible network. According to the rather gradual transitions of $[Fe(2\text{-}CH_3\text{-}phen)_3][ClO_4]_2$, this ability seems to be very well developed in such crystals [17, 42].

For a real system the transition curve will be found somewhere between the idealized lines. The more the system approaches the state of highest hierarchic order, the smaller will be the slope of the transition curve at the state of HDO (Fig. 4). It may therefore be proposed to consider the slope of the transition curve at the LS:HS ratio which corresponds to the STATE OF HDO of the system as a measure of the hierarchic order of the system under consideration. The greater the actual hierarchic order, the smaller should be the slope of the transition curve at the state of HDO.

General Considerations

It appears to the authors that these relationships may be considered as keynotes for the characterization of the hierarchic order of a given real system. Other keynotes may be provided by the so-called 'isokinetic relationship', which refers to the temperature at which the rates of homologous reactions are independent from the substituents at the reactants [43] or independent from the solvent [44, 45]. The alternative term 'compensation law' is based on the supposition that the proportionality constant β is positive, so that ΔH and ΔS change in the same direction, and the resulting variations of ΔG are less than they would be either by ΔH or ΔS alone. The proportionality constant β is called the 'isokinetic temperature', and a physical interpretation has been given. Temperature-independent chemical reactivity has been found recently in the course of a kinetic study: the rate constant for the decomposition of the intermediate involved in the reduction of pentacoordinated iron(III)–dimethylsulfoxide solvate is nearly independent of temperature, corresponding to the rate found only at the isokinetic point for other solvates [45].

The above considerations may in principle be valid for all phase transitions, and they may be important for other aspects for the development of materials science. We may learn to understand in what ways memory effects are preserved in order to prepare materials of desired properties. It seems also very likely that biological systems may be near the point of HDO, where maximal changes are possible by small changes in environment and by small changes in energy.

Finally it may be emphasized that the hierarchic order is not a preconceived idea of a new model, but rather a fundamental aspect of any given real system. It may even be stated that every real system must be subject to a hierarchic order, or in other words: *a system without hierarchic order would be incapable of existence* [46]. The authors suggest therefore that this point of view should be considered in all scientific investigations, so that these may lead to new questions, to new experiments and to new knowledge.

Acknowledgements

The authors are grateful to Professor Philipp Gütlich, Mainz, and to Professor Egon Uhlig, Jena, for having drawn their attention to these problems. They wish also to express their thanks to Professor D. N. Hendrickson, University of Illinois, Urbana, Ill., for the excahnge of views and results. Thanks are due to the Fonds zur Förderung der wissenschaftlichen Forschung in Österreich for partial support of this work through project No. 4428.

References

1 Part I: G. Resch and V. Gutmann, *Z. physik. Chem., (n.F.), 121,* 211 (1980).
2 Part II: G. Resch and V. Gutmann, *Z. physik. Chem. (n.F.), 126,* 223 (1981).
3 P. Gütlich, *Structure and Bonding, 44,* 83 (1981).
4 E. W. Müller, H. Spiering and G. Gütlich, *Chem. Phys. Letters,* to be published.
5 M. S. Haddad, M. W. Lynch, W. D. Federer and D. N. Hendrickson, *Inorg. Chem., 20,* 123 (1981).
6 M. S. Haddad, M. W. Lynch, W. D. Federer and D. N. Hendrickson, *Inorg. Chem., 20,* 131 (1981).
7 E. König and K. Madeja, *Inorg. Chem., 6,* 486 (1967).
8 I. Dészi, B. Molnár, T. Tarnoczi and K. Tompa, *J. Inorg. Nucl. Chem., 29,* 2486 (1967).
9 A. T. Casey and F. Isaac, *Austral. J. Chem., 20,* 2765 (1967).
10 P. Ganguli, P. Gütlich, E. Müller and W. Irler, *J. Chem. Soc. Dalton,* 441 (1981).
11 P. Gütlich, H. Köppen and H. G. Steinhäuser, *Chem. Phys. Lett., 74,* 475 (1980).
12 M. Sorai, J. Ensling, K. M. Hasselbach and P. Gütlich, *Chem. Phys., 20,* 197 (1977).
13 J. Fleisch, P. Gütlich and K. M. Hasselbach, *Inorg. Chem., 16,* 1979 (1977).
14 P. S. Rao, A. Reuveni, B. R. McGarvey, P. Ganguli and P. Gütlich, *Inorg. Chem., 20,* 204 (1981).
15 B. A. Katz and C. E. Strouse, *J. Am. Chem. Soc., 101,* 6214 (1979).
16 M. Greenaway, C. J. O'Connor, A. Schrock and E. Sinn, *Inorg. Chem., 18,* 2692 (1979).
17 H. A. Goodwin and R. N. Sylva, *Austral. J. Chem., 21,* 83 (1968).
18 P. Gütlich, R. Link and H. G. Steinhäuser, *Inorg. Chem., 17,* 2509 (1978).
19 H. G. Drickamer and C. W. Frank, 'Electronic Transitions and High Pressure Chemistry and Physics in Solids', Chapman Hill, London (1973).
20 D. C. Fisher and H. G. Drickamer, *J. Chem. Phys., 54,* 4825 (1971).
21 C. B. Bargeron and H. G. Drickamer, *J. Chem. Phys., 55,* 3471 (1971).
22 C. P. Slichter and H. G. Drickamer, *J. Chem. Phys., 56,* 2142 (1972).
23 P. Gütlich, Private Communication.
24 D. N. Hendrickson, Private Communication.
25 S. Stokka, K. Fossheim and S. Ziolkiewicz, *Phys. Rev., B24,* 2807 (1981).
26 M. Sorai and S. Seki, *J. Phys. Chem. Solids, 35,* 555 (1974).
27 M. Sorai and S. Seki, *J. Phys. Soc. Japan, 33,* 575 (1972).
28 J. H. Evans, *Nature, 229,* 403 (1971).
29 V. Gutmann and G. Resch, Bericht ATWD-18 (37. PTB-Seminar) Phys.-techn-Bundesanstalt Braunschweig (1981).
30 V. Gutmann, 'The Donor–Acceptor Approach to Molecular Interactions', Plenum, New York (1978).
31 C. Walsh, 'Enzymatic Reaction Mechanism', Freeman, San Francisco (1979).
32 Y. Fukuda and K. Sone, *J. Inorg. Nucl. Chem., 34,* 2315 (1974).
33 Y. Fukuda and K. Sone, *J. Inorg. Nucl. Chem., 37,* 455 (1975).
34 B. O. Sundström and H. Fischmeister, *Powder Met. Int., 5,* 171 (1973).
35 H. E. Exner, 'Grundlagen von Sintervorgängen', Metallkundlich-techn. Reihe, Ed. G. Petzow, Gebr. Bornträger, Berlin/Stuttgart (1978).
36 R. L. Hewitt, W. Wallace and M. C. Malherbe, *Powder Met. Int., 17,* 1 (1974).
37 N. Helliwell and P. J. James, *Powder Met. Int., 7,* 25 (1975).
38 V. Gutmann, G. Resch, R. Kratz and H. Schauer, *Z. anorg. allg. Chem., 491,* 95 (1982).
39 H. A. Goodwin and F. E. Smith, *Inorg. Nucl. Chem. Letters, 10,* 99 (1974).
40 G. Ritter, E. König, W. Irler and H. A. Goodwin, *Inorg. Chem., 17,* 224 (1978).
41 V. Gutmann and G. Resch, in 'Ions and Molecules in Solution', Eds. N. Tanaka *et al.,* Elsevier, London, in the press.
42 J. Fleisch, P. Gütlich, K. M. Hasselbach and W. Müller, *Inorg. Chem., 15,* 598 (1976).
43 O. Exner, *Progr. Phys. Org. Chem., 10,* 411 (1973).
44 R. Schmid and V. N. Sapunov, 'Non-formal Kinetics in Search for Chemical Reaction Pathways', Verlag Chemie, Weinheim/New York, (1982).
45 R. W. Soukup, R. Schmid, M. K. Arasteh and V. Gutmann, *Inorg. Chim. Acta, 73,* 21 (1983).
46 V. Gutmann and G. Resch, *Comments Inorg. Chem., 1,* 265 (1982).