Phase transitions in spin cross-over systems

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Phase transitions in spin cross-over systems

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Several complexes of iron and cobalt transform gradually or abruptly from a low-spin state to a high-spin state with increase in temperature and such transitions have been investigated widely in the past few years. Spin-state transitions in complexes are often accompanied by changes in enthalpy and crystal structure and many of them exhibit characteristics of first-order phase transitions. Transitions in certain complexes are affected by pressure, dopant metal ions and grinding and not infrequently show a plateau in the magnetic susceptibility-temperature plots. Seemingly unknown to coordination chemists, there is a fair body of information on the spin-state transitions in transition metal oxides and other extended solids. The transitions in rare earth cobaltates exhibit a plateau or a maximum in the inverse susceptibility-temperature plots, changes in enthalpy and crystal structure and other characteristics, not unlike those of the complexes. An attempt is made in this article, to bring together the essential features of spin-state transitions in metal complexes and oxides, particularly with respect to the nature of the phase transitions associated with spin cross-over. Models for spin-state transitions are examined and scope for further research indicated.

1. Introduction

Transition metal ions having electronic configurations d^4, d^5, d^6 or d^7 can exist in the low-spin or the high-spin ground state depending on the strength of the ligand field. When the field strength is close to the exchange energy corresponding to the cross-over of the ground state terms (Tanabe and Sugano 1954), a transition can occur between the two spin states. Such spin-state transitions are accompanied by changes in the magnetic susceptibility and other properties. Low-spin to high-spin transitions in complexes of iron and cobalt complexes have been investigated extensively in the past few years by employing magnetic susceptibility, heat capacity and spectroscopic studies. Mössbauer spectroscopy is especially effective for examining the transitions in Fe^{2+} complexes, the low- and high-spin states being associated with distinctly different isomer shifts. Spin-state transitions in complexes have been reviewed in the literature (Gütlich 1981 a) and the topic is of considerable relevance to the properties of cytochromes. Of particular interest to us in this article is the nature of the spin-state transition. In some complexes, the transition appears to be continuous while in others it is abrupt. Structural changes and enthalpy changes accompany the transition in many of the complexes and several explanations and models have been proposed to account for the varied features of these transitions. Spin-state transitions are by no means unique to transition metal complexes. They have been found in extended solids such as metal oxides, sulphides and other systems as well. Those who work with transition metal complexes however, seem to be unaware of the observations reported on metal

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oxide systems by solid state chemists (see, for example, Ramasesha *et al.* 1979) and yet the transitions in the two types of systems bear many similarities.

Spin-state transitions in metal oxides are by and large limited to those containing Co^{3+}. In particular, spin-state equilibria in cobaltates of the perovskite family have been investigated by emission Mössbauer spectroscopy, N.M.R. spectroscopy, X-ray photoelectron spectroscopy and a variety of other techniques (Rao 1984). Models have been proposed to account for the transitions in these oxides. The purpose of this article is to carry out a comparative study of the salient features of spin-state transitions in transition metal complexes and oxides and to examine the various models proposed to explain the occurrence of these transitions. We shall first describe the important experimental findings on spin-state transitions in iron and cobalt complexes as well as in transition metal oxides and attempt to offer explanations for some of the curious observations, where possible. We shall point out the nature of the phase transitions (Rao and Rao 1978, Rao 1984) accompanying spin-state transitions and briefly examine the various models with a view to finding common and essential features.

2. Transitions in iron and cobalt complexes

Low-spin⇌high-spin transitions are found to occur in several iron and cobalt complexes and the transitions in Fe(II) complexes between the $^5T_2$ and $^1A_1$ states have especially received much attention. The rate constants of the low- to high-spin transformations are generally of the order of 10^6 s^{-1} or more. The spin-state transition can be gradual or abrupt as shown in figure 1 and the energy difference between the
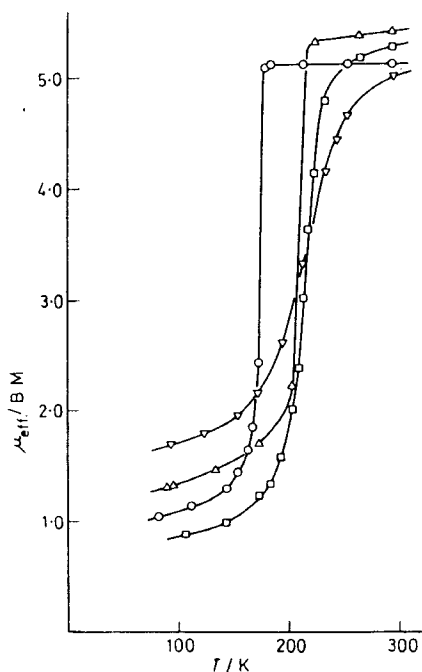
Figure 1.   Temperature variation of the magnetic moments of ferrous complexes showing gradual and abrupt transitions: triangles, [Fe(bt)₂(NC Se)₂]; squares, [Fe(bts)₂(NCS)₂]; circles, [Fe(bt)₂(NCS)₂] and inverted triangles, [Fe(btz)₂(NCS)₂] (from Bradley *et al.* 1978).

ground states of the two spin states in Fe complexes is between 500 and 1000 cm^{-1}. The abrupt or discontinuous transitions are generally accompanied by structural changes and thermal hysteresis is noticed in both the spin-state population and the unit-cell parameters (figures 2 and 3). The discontinuous spin-state transitions (König *et al.* 1979 a, b, 1982) generally seem to be first-order phase transitions (Rao and Rao 1978). Discontinuities in X-ray Debye–Waller factors also accompany the structural changes in these transitions. The exact nature of the structural change (symmetry, unit cell dimensions, etc.) has not been investigated in most of the complexes exhibiting spin-state transitions. It is well to remember that a change in unit cell parameters would be expected because of the difference in size of the high- and low-spin ions, but a change in symmetry need not necessarily occur.

Anomalous changes in heat capacity are found in complexes such as [Fe(Phen)$_2$(NCS)$_2$] undergoing abrupt changes in spin-state population (Sorai and Seki 1974). Some of the gradual transitions (see, for example, König *et al.* 1983) could be thermodynamically second order. Based on hysteresis effects, some complexes are reported to show characteristics of both first- and second-order transitions (Ganguli *et al.* 1981). Such conclusions may not however be altogether valid; the apparent absence of thermal hysteresis could be misleading and the magnitude of hysteresis may be rather small in some systems. If the enthalpy change of the transition is large, as for example in the case of [Fe(Phen)$_2$(NCS)$_2$], it has to be a first-order transition. Thermal hysteresis in phase transitions is known to depend on volume change, particle size and other factors (Rao and Rao 1966, Natarajan *et al.* 1969).

Some of the complexes show a plateau in the plots of magnetic moment or susceptibility against temperature as illustrated in figure 4. For example, in the case of Fe(III) complexes, instead of the μ_{eff} value varying between 5·9 μ_B ($^6A_1$) and 2·0 μ_B ($^2T_2$), a plateau is seen over a wide temperature range at an intermediate value of μ_{eff} (Haddad *et al.* 1981 a, b). An intermediate spin-state ($^4T_1$) has been proposed as a possible explanation, but it could be due to other causes. One possibility is the ordering of the low- and the high-spin states as found in LaCoO$_3$ (see §3 of this article).
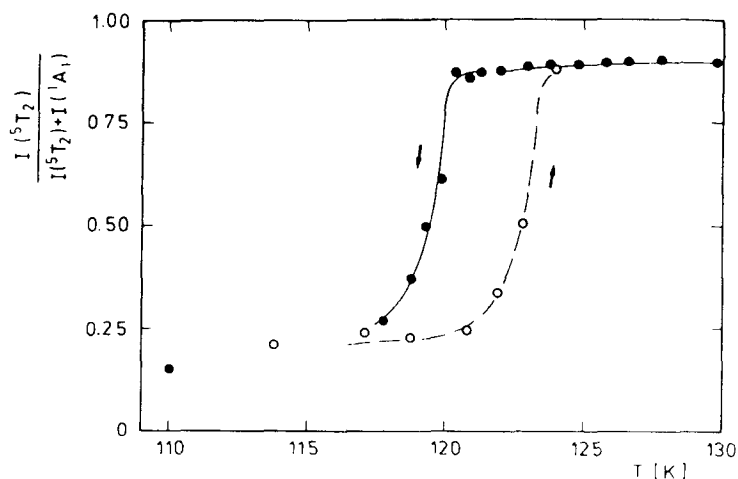

Figure 2. Temperature dependence of the relative intensity of X-ray diffraction lines of the high-spin state in [Fe(4,7-(CH$_3$)$_2$(Phen)$_2$(NCS)$_2$] near the transition temperature (from König *et al.* 1979 a).
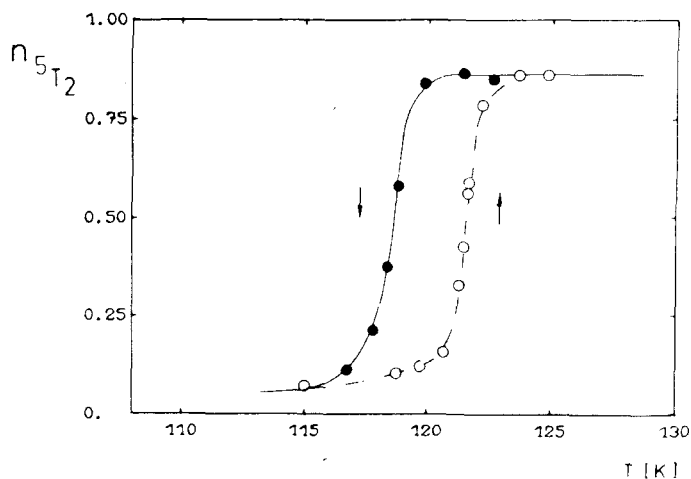
Figure 3. Temperature dependence on the high-spin fraction estimated from the Mössbauer
spectra of the same complex as in figure 2 (from König et al. 1979 a).
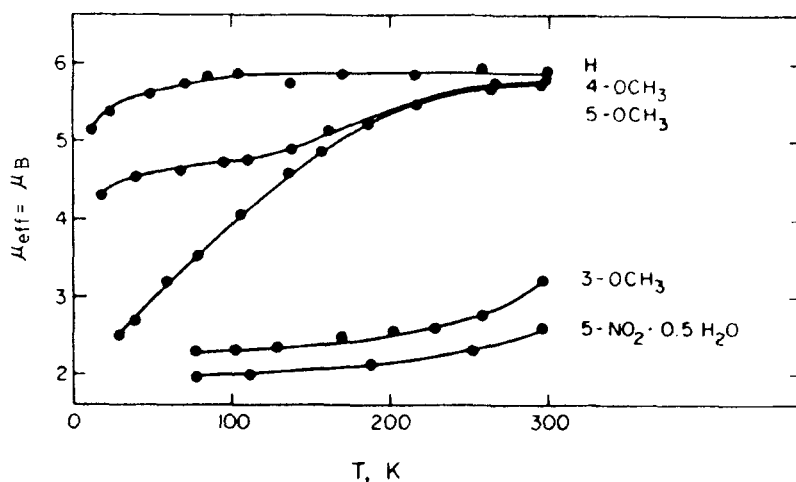
Figure 4. Temperature variation of the magnetic moments of $[Fe(R\text{-}Salmeen)_2](PF_6)$ for
different substituents, R (from Petty et al. 1978).

Recrystallization, grinding and molecules of solvation are all known to affect the
nature of spin-state transitions in complexes (Gütlich 1981 b, Haddad et al. 1981 a, b).
Accordingly, grinding has been found to make a transition gradual, leaving more low-
spin molecules at high temperatures. This has been considered to be due to defects, but
it is the feeling of the author that grinding could produce the same effects as the
application of high pressure. High pressure would favour the low-spin state.

Spin-state transitions are sensitive to doping by other metal ions. In complexes such
as $[Fe_xZn_{1-x}(2\text{-}pic)_3]Cl_2C_2H_5OH$, the nature of the spin transition depends on x
indicating the importance of the cooperative interaction between the electronic state of
the metal ion and the lattice (Gütlich 1981 b). What is more interesting is the

observation that doping affects the transition temperature markedly in some cases. Here again, pressure effects of dopant metal ions have to be borne in mind in understanding the observations. In the case of $[Fe(3\text{-}OCH_3\text{-}Sal\ Een)_2]PF_6$, doping with Cr^{3+} has only a small effect on the transition temperature, but substitution with Co^{3+} drastically increases the transition temperature (Haddad *et al.* 1981 b). This is probably because the radius of Co^{3+} (0·53 Å) is considerably smaller than that of Fe^{3+} and would be expected to have a positive pressure effect. Such pressure effects of dopant metal ions on phase transitions of solids are indeed well known (Rao and Rao 1978). For example, substitution of Gd^{3+} in place of Sm^{2+} in Sm S makes it metallic; the solid solution *on cooling, explosively transforms to a low-density structure. Substitution of* Cr^{3+} in place of V^{3+} in V_2O_3 has a negative pressure effect on the metal–insulator transition of V_2O_3. Partial substitution of Fe^{2+} by Mn^{2+} in $[Fe(Phen)_2(NCS)_2]$ drastically lowers the transition temperature. Mn^{2+} has a much larger radius (0·82 Å) than Fe^{2+} and would have a negative pressure effect; large Mn^{2+} concentration does indeed make the transition gradual (figure 5). Co^{2+} with a radius of 0·72 Å, on the other hand, has less marked effect on the transition; Zn^{2+} which has the same radius as Fe^{2+} has no effect. Residual paramagnetism at low temperatures in $[Fe_{1-x}M_x(Phen)_2(NCS)_2]$ can also be interpreted in terms of the relative size of the M^{2+} ion, the larger ionic size increasing the paramagnetism (Gütlich 1981 b). Such pressure effects of dopant metal ions are also found in Mn^{2+} substituted FeS_2 (Bargeron *et al.* 1971). Substitution of Fe in FeS_2 by Mn, stabilizes the high-spin state of Fe^{2+}; ordinarily, Fe in this sulphide is in the low-spin state. Application of pressure on $Fe_{1-x}Mn_xS_2$ results in a high-spin to low-spin transition. Obviously, one has to study the phase diagram and structures of such systems carefully before fully interpreting the results of ion substitution or application of pressure, since anomalous pressure effects on spin-state equilibria have been reported (Long *et al.* 1981).
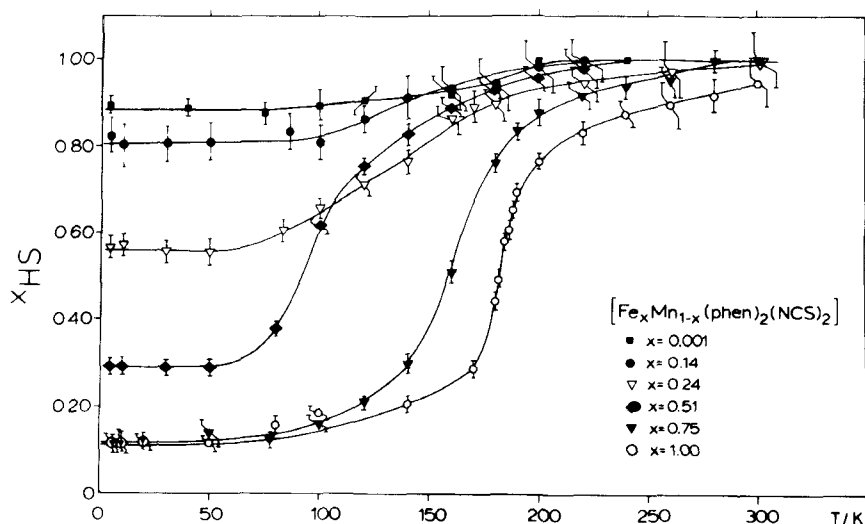

Figure 5. Temperature variation of the high-spin fraction of $[Fe_xMn_{1-x}(Phen)_2(NCS)_2]$ estimated from Mössbauer spectra (from Ganguli *et al.* 1982).

3.   Transition metal oxides

The rare earth cobaltates of the general formula $LnCoO_3$ ($Ln = La$, Y or any other lanthamide element) are by far the most extensively studied oxides with respect to spin-state equilibria (Raccah and Goodenough 1967, Bhide et al. 1972, 1973, Jadhao et al. 1975, 1976). In these oxides, Co^{3+} is in the low-spin t_{2g}^6 configuration at low temperatures and transforms to the high-spin state ($t_{2g}^4 e_g^2$) with increase in temperature (say up to 300–400 K). At higher temperatures, the behaviour depends on the rare earth ion; the lighter rare earth (La, Nd, etc.) cobaltates show evidence for charge-transfer between the low- and the high-spin states while the heavier rare earth (Ho, Er) cobaltates do not. We shall be mainly concerned here with the low- to high-spin transition rather than the charge-transfer effects. The spin-state transition in $LaCoO_3$ is quite unique in that the two spin states order themselves causing a change in symmetry from $R\bar{3}c$ to $R\bar{3}$. The ordering of the spin states in evidenced by a plateau in the inverse magnetic susceptibility-temperature curve (figure 6), such a behaviour having been noticed earlier in $MnAs_{1-x}P_x$ (Goodenough et al. 1965). The lighter rare earth cobaltates show thermal anomalies due to the spin-state transitions with ΔH values of around 400 J mol^{-1} or more; at the phase transition temperatures, changes in Debye–Waller factor, Lamb–Mössbauer factor and structural features are noticed. The heavier rare earth cobaltates do not show ΔH changes of this magnitude. It is interesting that at the transition temperatures, the low- to high-spin population ratio is generally unity.

Recently, it has been reported (Madhusudan et al. 1980) that the inverse susceptibility-temperature plots of $NdCoO_3$, $PrCoO_3$ and other cobaltates show a maximum (figure 7) and no plateau as in the case of $LaCoO_3$; the gradual variation of the magnetic moments in these cobaltates (figure 8) is not unlike that in the complexes discussed earlier. A study of the solid solutions of the type $La_{1-x}Nd_xCoO_3$ has shown a transition from the $NdCoO_3$-like behaviour (maximum in the $\chi^{-1}-T$ plot) to the $LaCoO_3$-like behaviour (plateau in the $\chi^{-1}-T$ plot) as shown in figure 9. This observation seems to suggest that we may be dealing with two extrema in behaviour of these spin cross-over systems. Furthermore, the spin-state transition temperature increases as we go across the rare earth series from La onwards (Ganguly and Rao 1980, Madhusudan et al. 1980). This may be because of the polarizing effect of the rare earth ion on the
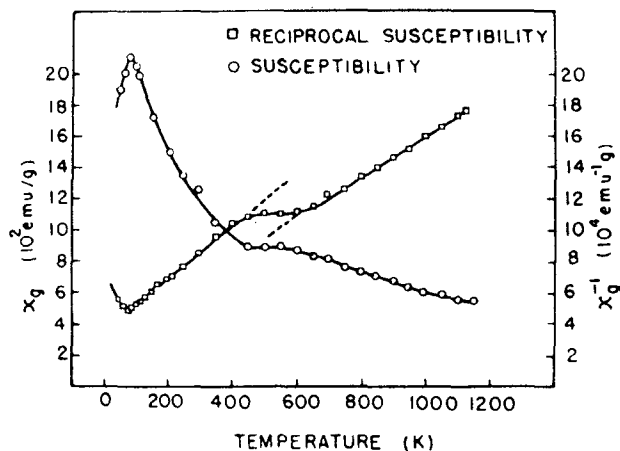
Figure 6.   Magnetic susceptibility behaviour of $LaCoO_3$ (from Bhide et al. 1972).
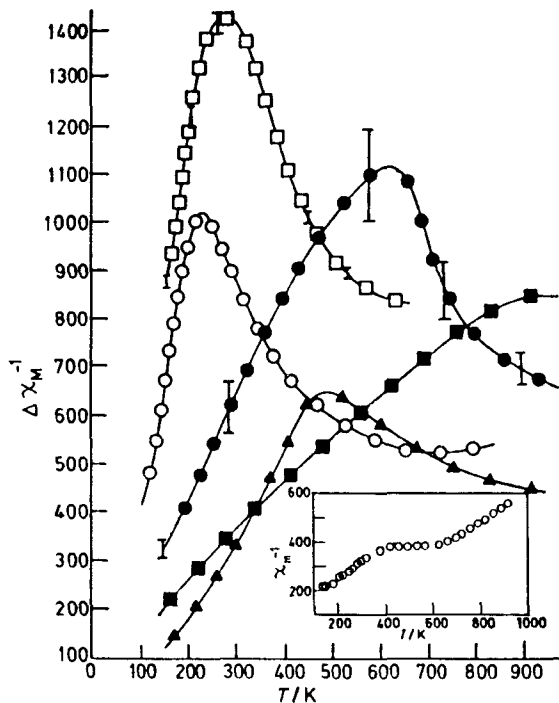
Figure 7. Plots of the cobalt contribution to the inverse susceptibility of rare earth cobaltates, $LnCoO_3$, against temperature: open circles, Pr; open squares, Nd; closed triangles, Tp; closed circles, Dy and closed squares, Yb. The curve of $LaCoO_3$ is shown in the inset (from Madhusudan *et al.* 1980).

Figure 8. Plots of the effective magnetic moments (of Co^{3+}) in $LnCoO_3$ against temperature. Arrows show the beginnings of the spin-state transitions. Notice the change in the spin-state transition temperature across the rare earth series. The transitions seem to be generally gradual and there is a finite population of the high-spin state at low temperature (from Madhusudan *et al.* 1980).

C. N. R. Rao

Figure 9. Temperature variation of the cobalt contribution to the inverse susceptibility of $La_{1-x}Nd_xCoO_3$: open circles, $x=1$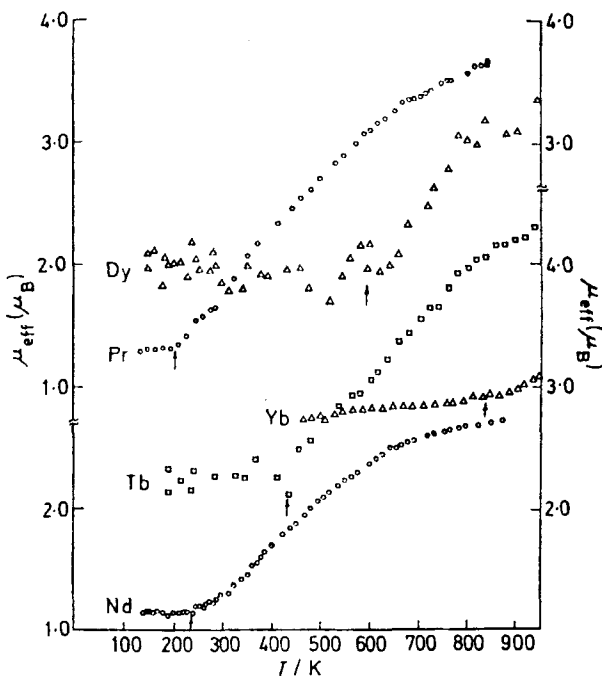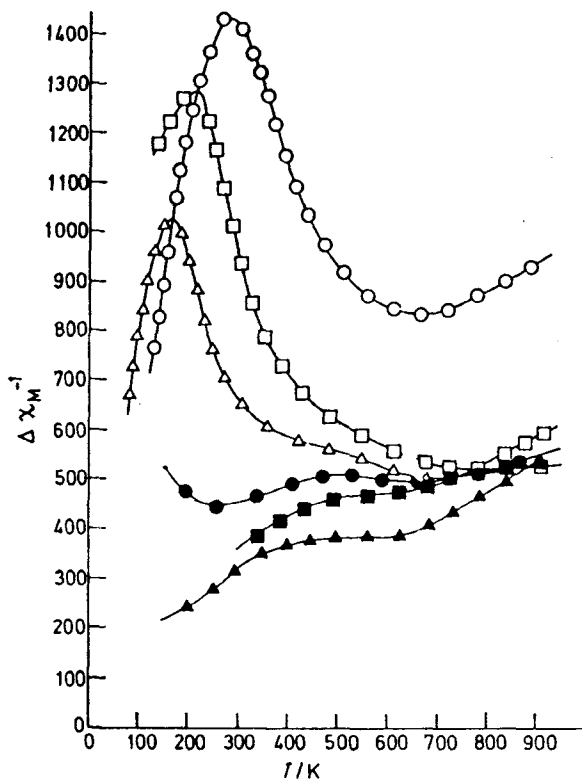; open squares, $x=0.8$; open triangles $x=0.6$; closed circles, $x=0.3$; closed squares, $x0.1$ and closed triangles, $x=0$ (from Madhusudan *et al.* 1980).

crystal field splitting, the latter increasing across the rare earth series accompanied by a decrease in the unit cell volume. The π^* orbital also would get significantly stabilized as we go across the series contributing to the increase in crystal field splitting. It must be noted however that the energy separation between the low- and the high-spin states in the cobaltates is in the range $100-500\,cm^{-1}$.

Chenavas and Joubert (1971) have reported a synthesis of Co_2O_3 under high pressure. The high-pressure phase seemed to consist of only low-spin Co^{3+} ions which on heating transformed to the high-spin state with a positive volume change of 6.7%. The results are suggestive of a first-order transition, but it is not entirely certain that a pure phase of Co_2O_3 was indeed prepared. It would be most worth while to investigate this oxide which has not hitherto been characterized.

The main features of the spin-state transitions of the various cobalt oxides that would have to be explained by any theoretical model are the following: (i) first-order as well as second-order phase transitions, the latter being accompanied by smaller ΔH values and a more gradual change in high-spin population, (ii) a change from $NdCoO_3$-like behaviour to $LaCoO_3$-like behaviour of the magnetic susceptibility, the latter being associated with a plateau, (iii) non-zero population of the high-spin state at very low temperatures exhibited by some systems, and (iv) spin-state population ratio of

unity around the transition temperature. The nature of the symmetry change in LaCoO$_3$ is also noteworthy; the high temperature phase is the ordered phase with lower symmetry.

Spin-state transitions have been noticed in quasi two-dimensional oxides of the K$_2$NiF$_4$ structure. La$_4$LiCoO$_8$ is one such oxide (Mohanram *et al.* 1983). It was first considered to show a maximum in the inverse susceptibility-temperature plot because of a low- to high-spin state transition of the Co^{3+} ions (Blasse 1965, Madhusudan *et al.* 1980). Demazeau *et al.* (1980) have interpreted the susceptibility data of La$_4$ LiCoO$_8$ (figure 10) in terms of the occurrence of low- to intermediate-spin and low- to high-spin transitions. In this oxide, the Li$^+$ and Co^{3+} ions are ordered in two dimensions (along the *ab* planes) as revealed by electron diffraction (Mohanram *et al.* 1983). Sr$_4$TaCoO$_8$ and Sr$_4$NbCoO$_8$ which possess the K$_2$NiF$_4$ structures show a susceptibility behaviour (figure 11) reminiscent of the plateau in the $\chi^{-1}-T$ plot of LaCoO$_3$. The Co^{3+} ions seem to transform from the low- to the intermediate-spin ($t_{2g}^5 e_g^1$) state in these oxides.

Demazeau *et al.* (1976, 1982) have reported that Ni^{3+} is in the low-spin $t_{2g}^6 e_g^1$ state in LaSrNiO$_4$, but in the high-spin $t_{2g}^5 e_g^2$ state in LaBaNiO$_4$. A magnetic susceptibility study of LaSr$_{1-x}$Ba$_x$NiO$_4$ has shown the e_g electrons in this system to be always in extended states forming a $\sigma_{x^2-y^2}^*$ band; with increase in x, the band width decreases accompanying an increase in the unit cell volume. While a small proportion of high-spin Ni^{3+} ions may be formed with increasing x, there appears to be no transition (Mohanram *et al.* 1983).
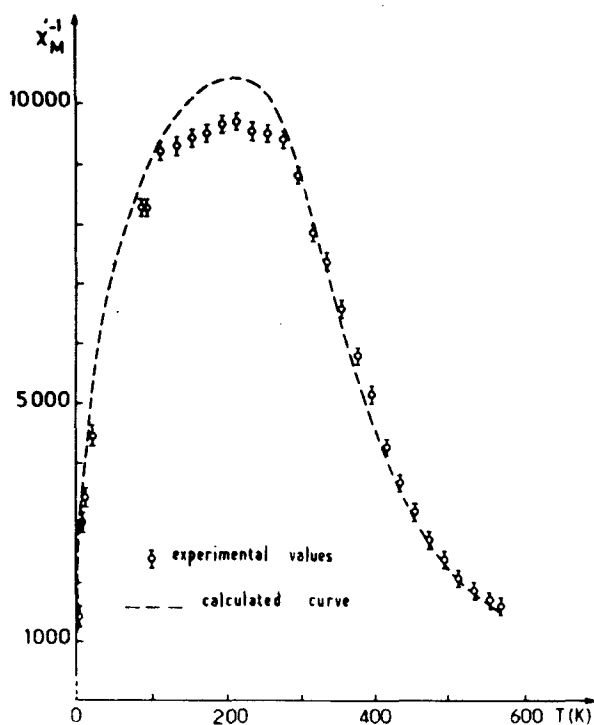

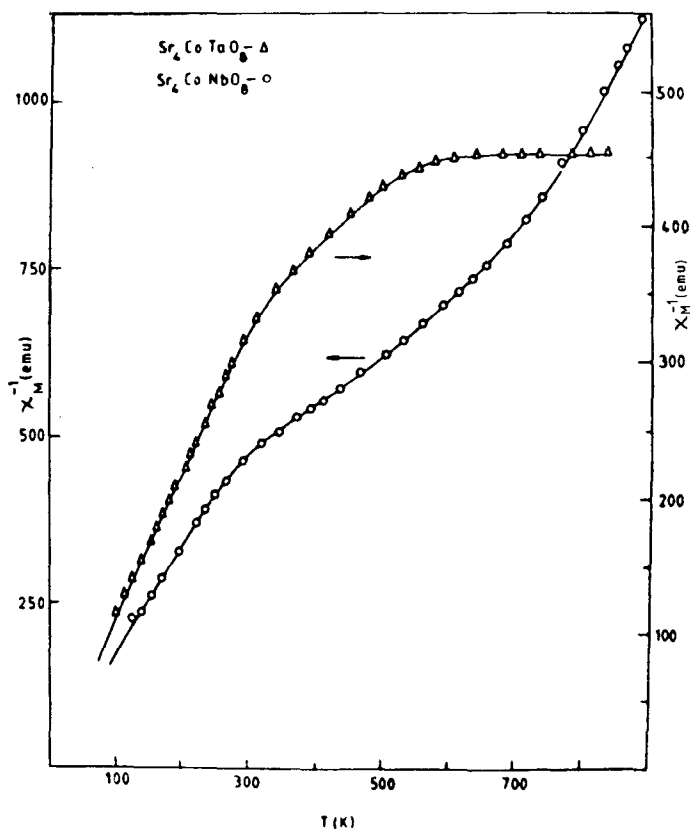Figure 10. Susceptibility behaviour of La$_4$LiCoO$_8$ (from Demazeau *et al.* 1980).

Figure 11. Inverse susceptibility-temperature curves of Sr_4CoTaO_8 and Sr_4CoNbO_8 (from Mohanram *et al.* 1983).

4. Theoretical models

The first model for spin-state transitions was proposed by Chesnut (1964) who gave a phenomenological description of systems containing triplet excitons such as TCNQ radical ion salts and Würster's blue perchlorate, in terms of the relatively high exciton concentrations. By treating the free energy as quadratically dependent on exciton concentration, Chesnut showed the occurrence of phase transitions in such systems. Wajnflasz and Pick (1971) assumed that transition metal ions can exist in two spin states, each with two different ionic radii and solved the hamiltonian in a molecular field approximation considering the interaction between ions to be of the Ising type. This model gave a first-order phase transition. König and Kremer (1971) analysed changes in the spin-state population semiempirically by assuming a temperature-dependent energy separation between the high- and low-spin states and a tetragonal distortion. Slichter and Drickamer (1972) provided an explanation for pressure-induced changes in the high-spin fraction of Fe(II) complexes by a treatment similar to that of Guggenheim's regular solution theory. Based on similar considerations, Sorai and Seki (1974) attempted to explain first-order spin-state transitions. The Gibbs free energy at a temperature was written by them as,

$$G = xG_{HS} + (1-x)G_{LS} + NkT\{x \ln x + (1-x) \ln(1-x)\} \tag{1}$$

where G_{HS} and G_{LS} are the Gibbs free energies of the high-temperature (high-spin) and low-temperature (low-spin) phases. The equilibrium mole fraction of the high-spin state, x, is given by,

$$x = 1/\{1 + \exp(\Delta G/NkT)\} \tag{2}$$

where $\Delta G (= G_{HS} - G_{LS})$ includes the vibrational term; the importance of the vibrational partition function had been pointed out earlier by Ewald *et al.* (1964). Sorai and Seki showed the spin-state transition to be cooperative, occurring through coupling between the electronic state of the metal ion and the phonon system; the strength of the coupling would determine the shape of the spin-state conversion curve, a weak coupling giving rise to a gradual conversion. In figure 12 the variation of the effective magnetic moment of [Fe(Phen)$_2$(NCS)$_2$] with temperature calculated from the additive equation (3) is compared with the experimental data of König and Madeja (1967).

$$\mu_{eff}^2 = x\mu_{eff}^2 \, (\text{HS}) + (1-x) \, \mu_{eff}^2 \, (\text{LS}) \tag{3}$$

The agreement is fairly good. The observed variation of the high-spin content with temperature in this complex is compared with that predicted by equation (2) in figure 13.

Gütlich *et al.* (1979) employed a phenomenological thermodynamic model to explain high-spin⇌low-spin transitions in complexes. According to this model, the transition occurs through a coupling between a primary spin change centre and $(n-1)$ neighbouring molecules undergoing secondary transitions. The size of such domains depends on the composition in a solid solution such as [Fe$_x$Zn$_{1-x}$(2−pic)$_3$]Cl$_2 \cdot$C$_2$H$_5$OH, the size increasing with x as given by $n(x) = 1 + n_0 x^\gamma$. Zimmerman and König (1977) had earlier made use of an interaction term such that the energies of the $^5T_2$ and $^1A_1$ states of ferrous complexes depend on the spin state of the neighbouring ions, in an Ising-type model; the magnitude of the
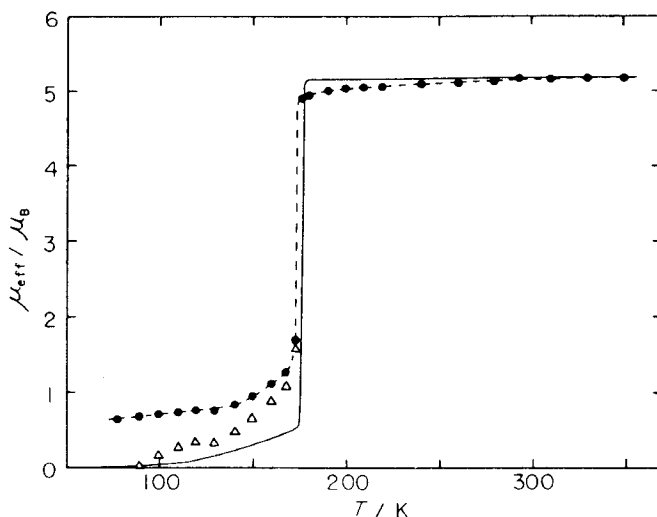

Figure 12. Temperature dependence of magnetic moment of [Fe(Phen)$_2$(NCS)$_2$]: solid line, calculated from equation (3); closed circles, experimental points of König and Madeja (1967); triangles, experimental values corrected for paramagnetic impurity content of 1·8% (from Sorai and Seki 1974).
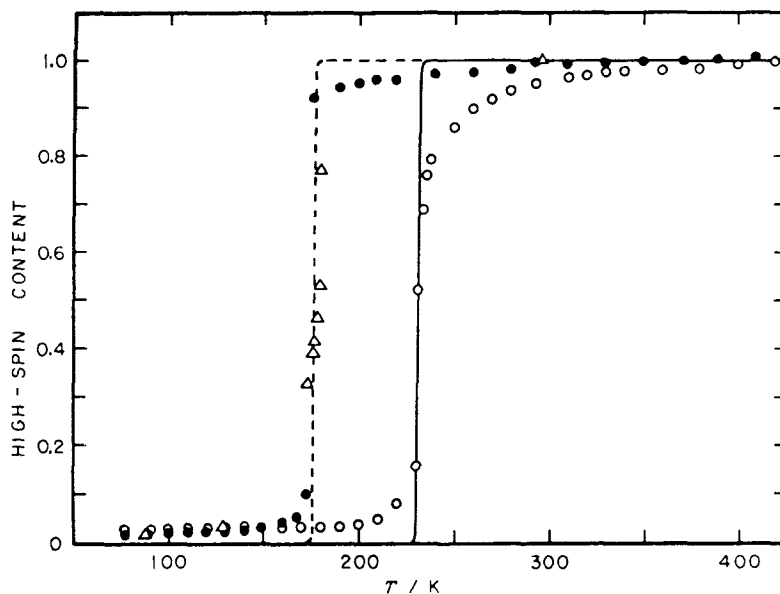
Figure 13. Temperature variation of the high-spin contents of $[Fe(Phen)_2(NCS)_2]$ and $[Fe(Phen)_2(NCSe)_2]$; calculated values from equation (2) are shown by broken and solid lines respectively. Experimental points are from magnetic moments and infrared spectra (from Sorai and Seki 1974).

interaction parameter J/kT_c determined when a transition occurred. Thus, a gradual transition resulted when $J/kT_c \geqslant 2$, for $T_c = 150$ K. In the domain model, on the other hand, the transformation occurs within the domains in which all the transition metal ions have the same spin. The parameter n (number of molecules per domain) is around 3·5 for a gradual transition and around 80 or 90 for an abrupt transition.

Spiering et al. (1982) have recently developed a model where the high-spin and low-spin states of the complex are treated as hard spheres of volume V_{HS} and V_{LS} respectively and the crystal is taken as an isotropic elastic medium characterized by bulk modulus K and Poisson constant σ_c. The complex is regarded as an inelastic inclusion embedded in a spherical volume V_c. The decrease in the elastic self-energy of the incompressible sphere in an expanding crystal leads to a deviation of the high-spin fraction (γ) from the Boltzmann population. The average free energy per molecule of the complex is written as

$$f = x[f_0 + \Delta(x)\gamma - \Gamma(x)\gamma^2] + (1-x)f_M \tag{4}$$

for a system such as $[Fe_xM_{1-x}(2-pic)_3]Cl_2 \cdot EtOH$ where the spin-state transition is influenced by the M ion. The terms Δ and Γ are interpreted in terms of the theory of elasticity as,

$$\Delta(x) = \Gamma(x) \cdot 2(V_{C,M} - V_{C,LS})/(V_{C,HS} - V_{C,LS}) \tag{5}$$

$$\Gamma(x) = x\frac{K}{2}\gamma_0(\gamma_0 - 1)(V_{HS} - V_{LS})^2/V_C \tag{6}$$

where V_Cs represents unit cell volumes of the corresponding pure compounds and

$\gamma_0 = 3(1 - \sigma_0)/(1 + \sigma_0)$. The coefficient Γ is the interaction parameter between high-spin molecules. The free energy per isolated molecule is given by,

$$f_0(T) = \gamma f_{HS}(T) + (1 - \gamma) f_{LS}(T) - T S_{mix} \tag{7}$$

Assuming a temperature-dependent energy splitting between the lowest LS and HS states, these workers have explained the gross behaviour of spin-state transitions of solid solutions of Fe^{2+} complexes (see also Sanner *et al.* 1984). It would be more interesting if such models could be used to explain the behaviour of systems where the radii of Fe^{2+} and M ions are considerably different (e.g. M = Mn) and affect the transition temperatures as well as the nature of the transition significantly. It is not clear whether such models would show a change from a gradual to abrupt transition depending on a meaningful parameter.

Kambara (1979) has proposed a microscopic model wherein the coupling between the *d* electrons and the lattice has been given a definitive meaning. Assuming that there is Jahn–Teller coupling between the *d*-electrons and the local intramolecular distortion. The hamiltonian of the system is written as

$$H = \sum_{i=1}^{N} h_i + \tfrac{1}{2} N M \omega^2 Q^2 \tag{8}$$

where h_i is the hamiltonian for a Fe^{2+} ion in the *i*th molecule and Q the displacement of the six ligands in the normal coordinate with the E_g symmetry of the O_h point group, M the effective mass and ω the frequency of the mode. The hamiltonian h_i is given by

$$h_i = h_0 + V_o + V_{so} + (\partial V / \partial Q)_0 Q + \tfrac{1}{2}(\partial^2 V / \partial Q^2)_0 Q^2 \tag{9}$$

where h_0 is the hamiltonian of the free ion, V_o the octahedral ligand field, V the ligand field due to the distorted molecule and V_{so} the spin–orbit interaction. The free energy per iron ion is represented as

$$F = -kT \sum_{i=1}^{3} g_i \exp(-E_i / kT) \tag{10}$$

and equilibrium Q values are found by minimizing F with respect to Q. Terms containing Q or Q^2 appear in the eigenvalues. The energy separation between the $^5T_{2g}$ and the $^1A_{1g}$ states (500–1000 cm^{-1}) in the undistorted phase is given by $E_0 = 20\,Dq - 5B - 8\,C$ where B and C are the Racah parameters. The Jahn–Teller coupling parameter, *a*, appearing in the expression for Q, is found by the relation, $E_{JT} = \tfrac{1}{2}a^2$ where $E_{JT} = 100–1000$ cm^{-1} and *a* is therefore between 0 and 50 cm$^{-1/2}$. In the linear coupling case (last term in equation (9) is zero), a first-order transition, with Q as the order parameter, occurs over a wide range of the coupling strength, *a*. If the second-order coupling is introduced, three possible kinds of the transition, with $Q > 0 \rightleftharpoons Q = 0$, $Q > 0 \rightleftharpoons Q < 0$ and $Q < 0 \rightleftharpoons Q = 0$, can occur. Phase transitions between high-spin states split by the distortion Q can also occur in addition to those between the low-spin and the high-spin states. The temperature variation of μ_{eff} calculated from equation (11) is in fair agreement for discontinuous spin-state transitions, when reasonable values of E_0 and *a* are employed (see figure 14)

$$\mu_{eff}^2 = \frac{kT}{N}(\chi_{\|} + 2\chi_{\perp}) \tag{11}$$

where χ is the magnetic susceptibility; the expression for χ includes E_i values which in turn are determined by E_0, *a*, Q and constants that relate the force constants and
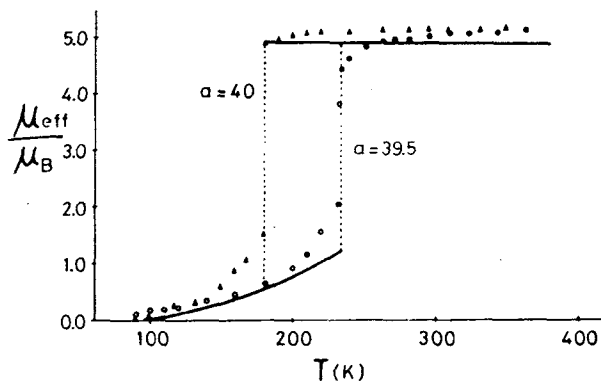
Figure 14. Temperature dependence of the magnetic moments of [Fe(Phen)$_2$(NCS)$_2$] and [Fe(Phen)$_2$(NCSe)$_2$] predicted by Kambara's model (1979) with $E_0 = 1000$ cm^{-1}. Experimental data of König and Madeja (1967) are shown as points.

vibrational frequencies. What is rather disappointing is that the agreement between theory and experiment from this treatment is not much different from that found with the simple equation (3).

Kambara (1981) has also treated intramolecular distortions as dynamical variables and taken intermolecular coupling into account. The effect of coupling between transition metal ions and a lattice strain has also been studied; the lattice would then drive the spin-state transition accompanying the cooperative intramolecular distortion even in the absence of strong coupling. When there is no distortion, the lattice strain varies continuously with temperature along with the spin-state. Discontinuous changes in the lattice strain occur with the cooperative intramolecular distortion over a narrow range of coupling strength. The results of the treatment with intermolecular coupling are similar to those from the static treatment (Kambara 1979), the only difference being in the meanings of the different parameters.

The hamiltonian in Kambara's second paper (1981) is

$$H = H_e + H_M + H_L + H_{eL} \qquad (12)$$

where H_e is the hamiltonian for d electrons of Fe ions in the undistorted system, H_M the hamiltonian for intramolecular displacements (which are coupled), H_L the elastic energy (which includes the bulk modulus and the square of the lattice strain) and H_{eL} the interaction between the d electrons and the lattice strain. The eigenvalues have terms representing elastic energy, displacement and the various coupling parameters including the Jahn–Teller coupling parameter given by $E_{JT} = (ja^2/2K_2)$. Thermal variation of μ_{eff} and of the population of the high-spin state show gradual or abrupt transitions as shown in figures 15 and 16 depending on the various parameters. Sasaki and Kambara (1982) have shown that a cooperative molecular distortion associated with a spin-state transition can be induced by a magnetic field. A small shift in the transition temperature of [Fe(Phen)$_2$(NCS)$_2$] seems to occur in the presence of a field of 5·5 T (Qi et al. 1983). This aspect is worthy of further investigation.

Bari and Sivardiere (1972) had earlier proposed a model for spin-state transitions based on Chesnut's model for the singlet–triplet transition in radical ion salts (Chesnut
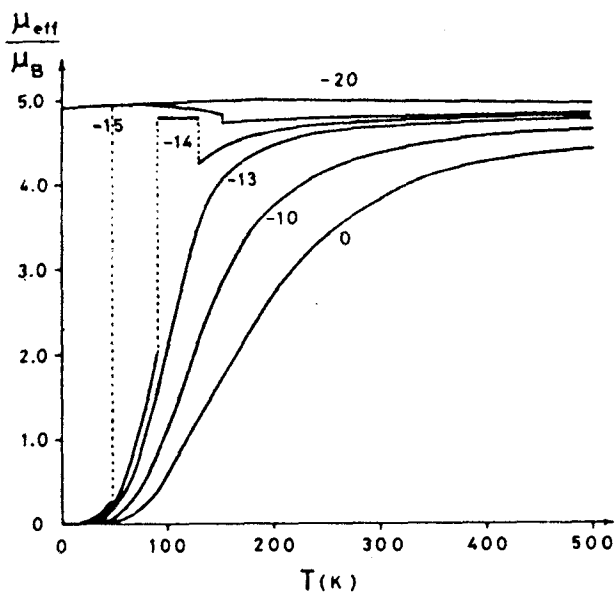
Figure 15. Temperature variation of the magnetic moment predicted by Kambara's model (1981) with $E_0 = 500 \, \text{cm}^{-1}$ and $a = 15 \, \text{cm}^{-1/2}$ for different values of the b parameter.
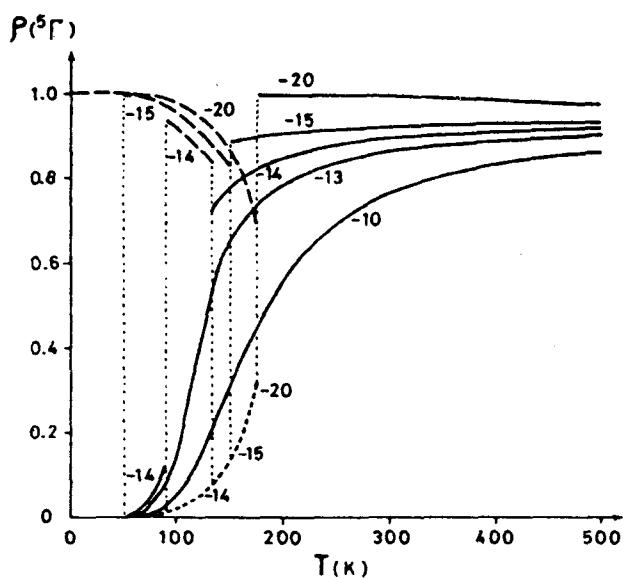

Figure 16. Temperature dependence of the relative populations of the high-spin states predicted by Kambara (1981). Solid, broken and dotted curves are for the $^5T_{2g}$, $^5B_{2g}$ and ^5E_g states respectively ($E_0 = 500 \, \text{cm}^{-1}$).

1964) which included the displacement of the breathing mode, Q, and the elastic constant in the hamiltonian

$$H = N\xi Q^2 + \sum_i (\Delta - VQ)n_i \tag{13}$$

Here, $(\Delta - VQ)$ represents the energy difference between the low- and the high-spin states and $n_i = 0$ and 1 for the low-spin and the high-spin states respectively. This model showed a first-order phase transition from the low- to the high-spin state with increasing temperature for $0.43 < (V^2/4\xi\Delta) < 1$. The ratio of the high-spin to the low-spin population saturated at $v:1$ where v is the multiplicity of the high-spin state. The model accounts for the transition in [Fe(Phen)$_2$(NCS)$_2$] to some extent. Bari and Sivardiere (1972) extended the model to include exchange interactions between the high-spin states leading to the prediction of heat magnetization; magnetic ordering has however not been observed in any of the systems showing spin-state transitions. Bari (1972) proposed a two-sublattice model to explain the structural transition accompanying the spin-state transition in LaCoO$_3$. The hamiltonian of Bari is given by

$$H = N\xi Q^2 + \sum_{iA} (\Delta - VQ)n_i + \sum_{iB} (\Delta + VQ)n_i \tag{14}$$

where the displacement on sublattice A is opposite to the displacement on sublattice B. This model shows a first-or second-order transition due to ordering followed by a spin-state transition of first or second order. Experimentally, the spin-state transition occurs before the ordering transition as one would expect. This study however points to the importance of elastic properties of the solid and of the coupling to a lattice distortion.

The models of Bari and Sivardiere are static and can be solved when the dynamics of the lattice are included. Ramasesha *et al.* (1979) have examined this problem and find that the dynamic model does not show a phase transition; this is true of the two-sublattice model as well. The dynamics of the lattice seem to wash away any phase transition arising from a static and linear coupling of the displacement to the spin states. A dynamic two-lattice model where the high-spin and the low-spin states are mixed by an ion-cage mode (with the transition metal ion moving off-centre with respect to the octahedral cage) however shows a non-zero population of the high-spin state at low temperatures. The coupling in this treatment is taken to be quadratic in displacement and the hamiltonian is written as

$$H = [(P_Q^2/2M) + \tfrac{1}{2}M\omega^2 Q^2]I + \Delta\sigma_z + \tfrac{1}{2}aQ^2 M\omega^2 \sigma_x \tag{15}$$

where ω is the vibrational frequency and σ represents the spin matrix. In figure 17 we show the inverse susceptibility-temperature curves predicted by this model while in figure 18 we show the predicted ratio of the high-spin to low-spin population as a function of temperature. Observation of a plateau in figure 17 and a non-zero population of the high-spin state in figure 18 is interesting, especially since these features have been found in both complexes and oxides. It was the objective of Ramasesha *et al.* (1979) to find models that would explain these two features as well as the first- or second-order phase transitions, with a spin-state population ratio of around unity near the transition.

The variation in the spin-state population shown in figure 18 is gradual. A coupling of the spin states to the cube of the sublattice displacement gives a first- or a second-order transition depending on the interaction parameter, but the high-spin state

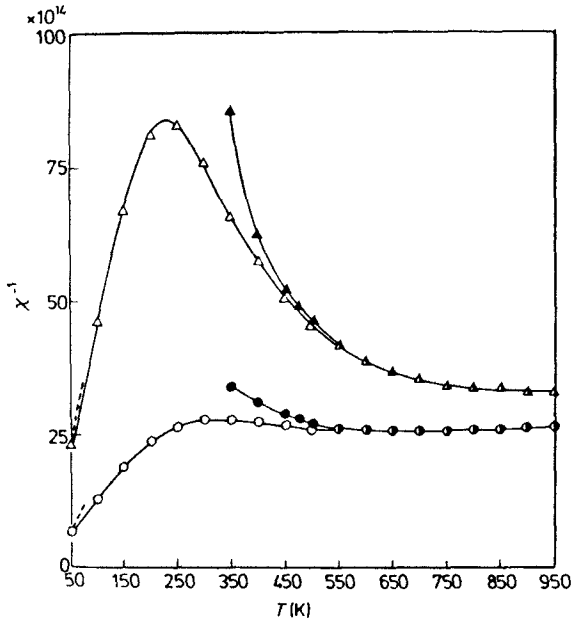Figure 17. Variation of the inverse susceptibility with temperature: open circles and triangles, from equation (15) with appropriate parameters; closed circles and triangles, from equation (16) with appropriate parameters (from Ramasesha *et al.* 1979).
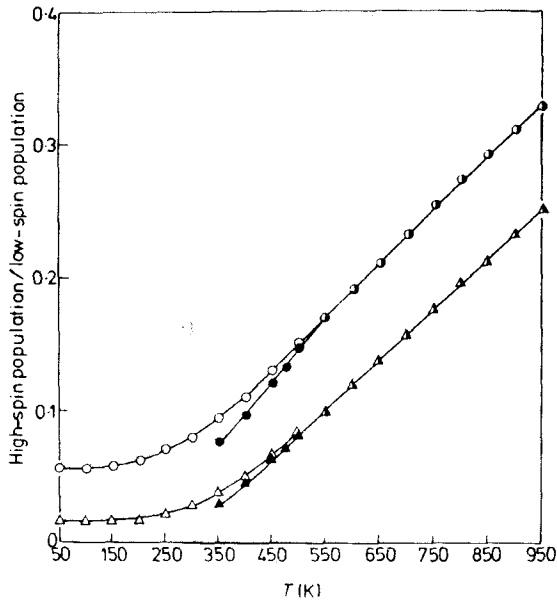

Figure 18. Temperature variation of the ratio of high-spin to low-spin population. Symbols are the same as in figure 17 (from Ramasesha *et al.* 1979).

population is always zero at low temperatures. It is possible to explain the different features of spin-state transition systems by including couplings of the spin states to the displacements of a breathing mode and an ion-cage mode, the former being linear and the latter, quadratic. The ion-cage mode would mix the spin states. The hamiltonian describing this model is given by

$$H = \sum \left[\left(\frac{P_{Q_i}^2}{2M} i + \frac{P^2 x_i}{2M} + \frac{1}{2} M\omega_b^2 Q_i^2 + \frac{1}{2} M\omega^2 X_i^2 \right) I + (\Delta + V Q_i)\sigma_z + a X_i^2 \sigma_x \right] \quad (16)$$

where ω_b and ω are the frequencies of the breathing and ion-cage modes respectively and a, V and Δ are the coupling strengths. In solving equation (16), the breathing mode displacement, Q_i, was treated classically. This model tends to the linear two-sublattice model in the limit $a \to 0$. The spin-state transition can be gradual or abrupt and the high-spin population can be non-zero as $T \to 0$. The variation in spin-state population predicted by this model is more abrupt (figure 18) and the inverse susceptibility shows a steeper maximum before saturation (figure 17). The two-phonon model given by equation (16) should be able to explain all the features of spin-state transitions including a structural phase transition accompanying the spin-state transition. It is worth exploring this model further. Certain similarities between this model and the models of Kambara (1981) are apparent and it appears that any microscopic model that attempts to explain the known features of spin-state transitions would have to include coupling of the displacement of the octahedra (even if treated classically) and also possibly a dynamic term for mixing the spin state.

5. Scope for further study

In an area of this kind, there are many obvious aspects that would require further study. We shall indicate a few of those aspects that are of interest to the author.

(i)   Although thermal anomalies and changes in X-ray diffraction patterns have been observed to accompany spin-state transitions, detailed structural studies with regard to changes in symmetry and other structural aspects are lacking. This is specially true of rare earth cobaltates other than $LaCoO_3$ where it is not entirely certain that symmetry or structural changes occur at the spin-state transitions. Since single crystal specimens of many of the oxides may be difficult to prepare, X-ray or neutron profile analysis with powder diffraction patterns recorded at different temperatures would be worth while.

(ii) The nature of the gradual (or second-order!) transitions has to be studied, including the critical behaviour and soft modes if any.

(iii) Mixed-order transitions in complexes as well as complexes showing a plateau in magnetic measurements have to be understood; oxides showing a plateau also need to be studied further.

(iv) Combined pressure and metal ion substitution experiments would be interesting in the case of complexes. Pressure experiments on oxide systems would be equally useful; efforts should be made to prepare pure, the hitherto unknown, Co_2O_3 at high pressures.

(v)   The 'order' of the spin-state transition(s) in $LaCoO_3$ seems to depend on the method of preparation. The origin of this is not clear.

(vi) It should be interesting to investigate transitions in complexes and other derivatives of Ni^{3+} and such ions.

(vii) Effect of high magnetic fields on the transitions needs to be investigated. Use of solid state N.M.R. to study spin-state transitions, especially in oxides, should be explored.

(viii) Although various models exist, it would be fruitful to put together a simple unifying model which would explain most of the important features of the transitions in oxides and complexes. This should not be difficult in the light of the knowledge already gained from the available models.

Acknowledgment

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