

## TEMPERATURE AND PRESSURE-INDUCED SPIN-STATE TRANSITIONS: APPLICATIONS OF HIGH-RESOLUTION X-RAY SPECTROSCOPY

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The spin state of the transition metal compounds is a major parameter determining the material's chemical and physical properties. The properties may be as different for different spin states as if the metal ion were replaced by a different element. The metal ion in octahedral surroundings with electron configuration  $d^4 \dots d^7$  can exist in low spin (LS) or high spin (HS) state, depending on the energy separation of the  $t_{2g}$  and  $e_g$  levels caused by the crystal field [1, 2]. Upon external conditions, such as temperature, applied pressure, or strong magnetic field, irradiation by light, *etc.* the spin state of a compound may revert. With the spin state transition most physical and chemical properties of the system change, including bond lengths, multiplicity, density, electronic and heat transport properties. Determination of the spin state is therefore crucial in many fields, including inorganic and organometallic chemistry, solid state and geosciences. In a number of molecular systems of medium ligand field strength, the spin state can be switched back and forth between the LS and the HS states by triggering a redistribution of the  $3d$  electrons on the  $t_{2g}$  and  $e_g$  levels [2]. The spin state can also change upon temperature in certain oxides with strongly correlated electrons: a prominent example being  $\text{LaCoO}_3$ , in which the  $\text{Co}^{3+}$  ions in octahedral environment undergo two broad magnetic transitions, the one at higher temperature being accompanied by a metal-insulator transition. These transitions in  $\text{LaCoO}_3$  involve the change of the spin state; however, the nature of the transition is still debated [3,4]. Being crucial to the transport properties, knowledge of the spin state in such oxides is indispensable to the understanding the electronic structure [5]. In addition to thermal effects, external pressure often causes spin state transitions. In systems exhibiting temperature-induced transitions, this occurs at relatively low ( $\approx 10$  kbar) pressures [2, 3]. Shrinking of bond length is accompanied by rapid increase in the ligand-field splitting ( $10 Dq \propto r^{-5}$ ), therefore even compounds exhibiting high spin state at ambient conditions undergo a spin state transition to LS state at high enough pressures [6–10].

Sample environments necessary for extreme conditions or the presence of different magnetic components in the sample might limit or hinder the use of conventional techniques to determine the spin states of the transition metal in compounds. Element selective techniques with highly penetrating hard X rays therefore find numerous applications in determining the total spin momentum of the transition metal.

Hard X-ray spectroscopies fulfil all criteria to probe the spin state in the bulk [11–14]. In order to demonstrate the above we have conducted systematic investigations on spin transition complexes of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Co}^{2+}$  (well below and above their transition temperatures) [15,16]. As we shall see, these molecular compounds cover almost the entire  $d^4 \dots d^7$  range, have unambiguous spin states and show diverse spin transitions. As an example, the effects of the thermally induced transitions will be shown by X-ray spectra of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , a widely studied family of spin-transition complexes, with a  $3d^6$  central ion. The compound exhibits a  ${}^1A_{1g}$  ( $t_{2g}^6 e_g^0$ ,  $S=0$ , LS) to  ${}^5T_{2g}$  ( $t_{2g}^4 e_g^2$ ,  $S=0$ , HS) transition at 178 K. The full K-emission spectrum of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  is displayed in Figure 1 for both HS and LS states. As it is seen, all emission features undergo a relevant modification upon the change in the spin state. The  $K\beta$  intensity drops in the  $K\beta'$  satellite region when the  $3d$  spin momentum is diminished. The variation of the  $K\alpha$  line shape is more complex, but the differences are substantial. The sensitivity of the  $K\alpha$  ( $K\beta$ ) emission lines arise from the exchange interaction between the  $2p$  ( $3p$ ) core hole and the unpaired  $3d$  electrons in the final state. The large spatial overlap of the  $3d$  orbitals with the  $3p$  core hole results in a large  $3p3d$  exchange coupling, which leads to a splitting as high as 15 eV. Beside this dominant feature, manifested in the clear separation of the  $K\beta'$  satellite, the spectrum is influenced by other interactions, too. Due to a smaller overlap, the  $2p3d$  exchange coupling is smaller, which leads to a splitting of 1-2 eV in the  $K\alpha$  spectrum. This is in the range of the line width of the  $K\alpha$  lines, therefore, the change in the spin state appears as a mere variation of the line broadening. Thus, while the total variation of the  $K\alpha$  spectrum is bigger than that of the  $K\beta$ , as it is evident from the spectra in Figure 1, the interpretation of the  $K\beta$  spectra is more straightforward. An additional advantage of the  $K\beta$  is its higher energy especially in case of strongly absorbing samples or sample environments.

The highest energy features in Figure 1,  $K\beta''$  and  $K\beta_{2,5}$ , emerge due to valence electrons filling the  $1s$  core hole; their final states are identical to those in photoelectron spectroscopy, thus prominent chemical sensitivity is expected in this spectral region [11]. These peaks are also modified upon the spin transition; however, the spectral variations stem from the changes in the bonding. Being weak and unrelated to the spin

momentum, these high energy lines are of little use as probes of the spin state.

In the spin transition regime the XES spectra were shown to consist of superposed HS and LS states [17, 16, 18]. This allows a precise determination of the HS fraction for two-state transitions [16], and has been exploited in several studies [3, 10, 18, 19]. Reassuringly, XES and soft X-ray absorption spectroscopy (XAS) gave similar results for the less unambiguous transitions of  $\text{LaCoO}_3$ , [3, 4] (see Figure 2). XES with careful line-shape analysis is becoming an established probe of the spin state [16, 7, 18].

As the rearrangement of the electrons at the spin transition affects the electronic structure and the local geometry, XAS can also be used to follow spin transitions. K-edge X-ray absorption was applied by several authors to study structural variations accompanied by the spin transition, or to follow the evolution of the transition [12, 13]. The pre-edge region, stemming from  $1s \rightarrow 3d$  transitions (in case of an octahedral environment), is expected to be most sensitive to the spin state, since the variation in the  $3d$  populations obviously change the density of states and the electron-electron interaction energies alike. However, due to its quadrupolar origin, this spectral region is of low intensity, not well separated from the edge tail, poorly resolved, therefore little effort has been made to explore spin states from such spectra. Better separation of the pre-edge features is achieved by combining XAS with XES. This technique, the resonant X-ray emission spectroscopy (RXES), provides details on the redistribution of electrons on the  $3d$  levels associated with the spin-state transition. It reveals features at the X-ray absorption pre-edge that are hardly accessible through standard XAS measurements; this is clearly demonstrated in Fig. 3 with spectra of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ .

In addition to the above techniques, non-resonant inelastic X-ray scattering has proven great potential in studying  $d-d$  excitations [20]; therefore, it can open new opportunities in spin state studies.

Finally, we report on hard X-ray induced excited spin-state trapping (HAXIESST) in  $[\text{Fe}^{\text{II}}(\text{phen})_2(\text{NCS})_2]$  [21]. In Figure 4, results of a rapid energy scan are displayed at 30 K, far below the transition temperature, reflecting an LS state. However, according to a second, longer scan by the intense X-ray beam an anomalous metastable HS state appears to form. Previously green light had been found to populate the metastable low-temperature HS state of this molecule; a phenomenon called light-induced excited spin-state trapping (LIESST). This switching to the HS state proceeds through several excited states; the excitation and relaxation mechanisms are determined by the strongly coupled electron, magnetic, and structural dynamics. With a certain branching ratio the molecule transforms to the HS state. The relevant vibrational modes being inactive, non-adiabatic multi-phonon relaxation is hindered below 50 K, which leads to a very small HS $\rightarrow$ LS tunnelling rate [22]. At higher temperatures, where the higher vibrational states of the HS become populated, the relaxation speeds up as a result

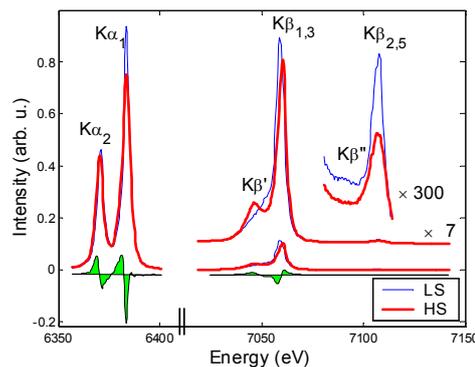


Figure 1. Full K-emission spectra of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  in the HS (thick line) and LS (thin line) state. The  $\text{K}\beta$  and the valence emission regions are also shown in magnified forms. Below the spectra, the shaded area displays the HS-LS spectral difference.

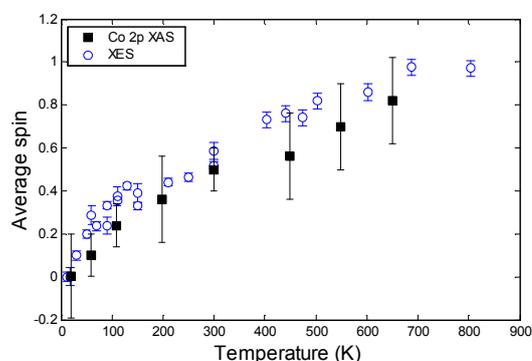


Figure 2. Temperature evolution of the average cobalt spin momentum in  $\text{LaCoO}_3$ . The analysis based on the XES data [3] is in fair agreement with the results obtained from  $L_{2,3}$  spectroscopy [4].

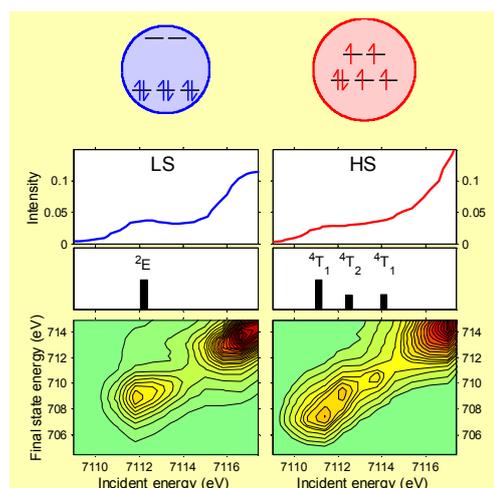


Figure 3. Top: The pre-edge region of the Fe K absorption edge of  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  [12]. Middle: transitions predicted by multiplet theory. Bottom:  $1s2p_{3/2}$  RXES spectra. (Above the spectra the distribution of the  $3d$  electrons on the  $t_{2g}$  and  $e_g$  levels is shown.)

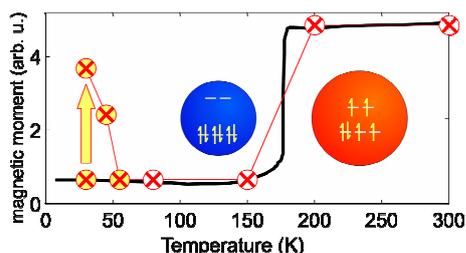


Figure 4. Magnetic moment of  $[\text{Fe}^{\text{II}}(\text{phen})_2(\text{NCS})_2]$  determined from X-ray emission data (circles with symbol X) and from conventional magnetization measurements (solid line).

of a larger overlap of the higher lying vibrational wavefunctions of both spin states. The remarkably similar temperature dependence of the metastable HS population created by light and X-rays suggest similar relaxation mechanisms. While the low- $T$  HS state and its decay conditions are the same in LIESST and HAXIESST, the excitation is obviously different: visible light can induce the necessary ligand-field excitations, unlike the hard X-rays. The spin-state trapping occur via relaxation processes that follow electronic excitations caused mostly by secondary electrons. Irradiation with hard X-rays may populate metastable states even when optical excitation is limited by sample characteristics or by its environment, as in the cases of non-transparent samples or cells for extreme conditions. This result unveils the non-innocent nature of low-temperature hard X-ray investigations, where spectroscopy or diffraction experiments might lead to excitations similar to visible light-induced excitations.

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## References

- [1] S. Alvarez, J. Cirera, "How high the spin? Allowed and forbidden spin states in transition-metal chemistry" *Angew. Chem. Int. Ed.* **45** (2006) 3012–3020.
- [2] *Spin Crossover in Transition Metal Compounds I-III*, in: *Topics in Current Chemistry*, P. Gütllich, H.A. Goodwin, (Eds.), (Springer, Berlin-Heidelberg 2004) Vols. 233-235.
- [3] G. Vankó, J.-P. Rueff, A. Mattila, Z. Németh, A. Shukla, "Temperature and pressure-induced spin-state transitions in  $\text{LaCoO}_3$ ", *Phys. Rev. B* **73** (2006) 024424.
- [4] M.W. Haverkort, Z. Hu, J.C. Cezar, T. Burnus, H. Hartmann, *et al.*, "Spin state transition in  $\text{LaCoO}_3$  studied using soft x-ray absorption spectroscopy and magnetic circular dichroism", *Phys. Rev. Lett.* **97** (2006) 176405.
- [5] A. Maignan, V. Caignaert, B. Raveau, D. Khomskii, G. Sawatzky, "Thermoelectric power of  $\text{HoBaCo}_2\text{O}_{5.5}$ : possible evidence of the spin blockade in cobaltites", *Phys. Rev. Lett.* **93** (2004) 026401.
- [6] J.-P. Rueff, C.-C. Kao, V.V. Struzhkin, J. Badro, J. Shu, R.J. Hemley, H.K. Mao, "Pressure induced high-spin to low-spin transition in FeS evidenced by x-ray emission spectroscopy", *Phys. Rev. Lett.* **82** (1999) 3284–3287.
- [7] J.-P. Rueff, A. Shukla, A. Kaprolat, M. Krisch, M. Lorenzen, F. Sette, R. Verbeni, "Magnetism of Invar alloys under pressure examined by inelastic x-ray scattering", *Phys. Rev. B* **63** (2001) 132409.
- [8] J. Badro, G. Fiquet, F. Guyot, J.-P. Rueff, V.V. Struzhkin, G. Vankó, G. Monaco, "Iron partitioning in the earth's lower mantle; toward a deep lower-mantle discontinuity", *Science* **300** (2003) 789–791.
- [9] J. Badro, J.P. Rueff, G. Vankó, G. Monaco, *et al.*, "Electronic transitions in perovskite: possible non-convecting layers in the lowermost mantle", *Science* **305** (2004) 383–386.
- [10] J.-F. Lin, G. Vankó, S.D. Jacobsen, V. Iota, V.V. Struzhkin, V.B. Prakapenka, *et al.*, "Spin transition zone in Earth's lower mantle", *Science* **317** (2007) 1740–1743.
- [11] P. Glatzel, U. Bergmann, "High resolution 1s core hole x-ray spectroscopy in 3d transition metal complexes - Electronic and structural information", *Coord. Chem. Rev.* **249** (2005) 65–95.
- [12] V. Briois, C. Cartier dit Moulin, P. Sainctavit, C. Broder, A.-M. Flank, "Full multiple scattering and crystal field multiplet calculations performed on the spin transition  $\text{Fe}^{\text{II}}(\text{phen})_2(\text{NCS})_2$  complex at the iron K and  $L_{2,3}$  X-ray absorption edges", *J. Am. Chem. Soc.* **117** (1995) 1019.
- [13] C. Hannay, M.-J. Hubin-Franskin, F. Grandjean, V. Briois, J.-P. Itié, A. Polian, S. Trofimenko, G.J. Long, "X-ray absorption spectroscopic study of the temperature and pressure dependence of the electronic spin states in several iron(II) and cobalt(II) tris(pyrazolyl)borate complexes", *Inorg. Chem.* **36** (1997) 5580–5588.
- [14] K. Tsutsumi, H. Nakamori, K. Ichikawa, "X-ray Mn K $\beta$  emission spectra of manganese oxides and manganates", *Phys. Rev. B* **13** (1976) 929–933.
- [15] G. Vankó, T. Neisius, F. Renz, A. Shukla, F. de Groot *et al.*, "Molecular spin transitions studied with X-ray emission spectroscopy", *ESRF Highlights* 2002, pp. 59–60.
- [16] G. Vankó, T. Neisius, G. Molnár, F. Renz, S. Kárpáti, A. Shukla, F.M.F. de Groot, "Probing the 3d spin momentum with x-ray emission spectroscopy: the case of molecular spin transitions", *J. Phys. Chem. B* **110** (2006) 11647.
- [17] X. Wang, F.M.F. de Groot *et al.*, "Spin-polarized x-ray emission of 3d transition-metal ions: A comparison via K $\alpha$  and K $\beta$  detection" *Phys. Rev. B* **56** (1997) 4553.
- [18] G. Vankó, F.M.F. de Groot, "Comment on « Spin crossover in  $(\text{Mg,Fe})\text{O}$ : A Mössbauer effect study with an alternative interpretation of x-ray emission spectroscopy data »", *Phys. Rev. B* **75** (2007) 177101.
- [19] R. Lengsdorf, J.-P. Rueff, G. Vankó, T. Lorenz, L.H. Tjeng, M.M. Abd-Elmeguid, "Spin-state-driven metal-insulator transition in  $(\text{La,Sr})\text{CoO}_3$  under high-pressure", *Phys. Rev. B* **75** (2007) 180401.
- [20] M.W. Haverkort, A. Tanaka, L.H. Tjeng, G.A. Sawatzky, "Nonresonant inelastic x-ray scattering involving excitonic excitations: The examples of NiO and CoO", *Phys. Rev. Lett.* **99** (2007) 257401.
- [21] G. Vankó, F. Renz, G. Molnár, T. Neisius, S. Kárpáti, "Hard X-ray induced excited spin-state trapping" *Angew. Chem. Int. Ed.* **46** (2007) 5306–5309.
- [22] A. Hauser, "Light-induced spin crossover and the high-spin  $\rightarrow$  low-spin relaxation", *Top. Curr. Chem.* **234** (2004) 155, and references therein.