Character of the excited state of the Co^{3+} ion in $LaCoO_3$

Character of the excited state of the Co^{3+} ion in $LaCoO_3$

K Knížek, Z Jirák, J Hejtmánek and P Novák

Institute of Physics ASCR, Cukrovarnická 10, 162 53 Prague 6, Czech Republic

Abstract
Generalized gradient approximation (GGA) $+ U$ calculations for $LaCoO_3$
confirm the existence of a stationary state composed of a mixture of the low
spin (LS) and high spin (HS) Co^{3+} ions in a 1:1 ratio, which is of insulating
character. At low temperatures, this state is located about 25 meV above the
homogeneous LS ground state if Co_{LS}–O–Co_{HS} bond length optimization is
taken into account. The energy difference decreases with the lattice dilatation
and the LS + HS(1:1) phase with bond length optimization becomes stable at
some intermediate temperature. These results, together with previous electron
spin resonance evidence for HS excitations in the LS ground state, lead to
the conclusion that the diamagnetic–paramagnetic transition in $LaCoO_3$ at 50–
150 K is caused by a gradual population of HS Co^{3+} ionic states, provided
that neighbouring sites are in the LS state. Consistency between experimental
data for the paramagnetic susceptibility and anomalous thermal expansion is
achieved for an HS–LS energy difference of 16 meV that corresponds to 180 K.
With increasing HS population, the antiferromagnetic (AF) interactions HS–
LS–HS become effective. The LS + HS(1:1) phase is saturated above 150 K
and the susceptibility acquires a simple Curie–Weiss behaviour in which AF
interactions are characterized by $\theta = -160$ K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

At low temperatures the cobaltite $LaCoO_3$ is nonmagnetic, the Co^{3+} ion being in the low spin
(LS) state that in the limit of fully localized electrons in a strong crystal field corresponds to
filled t_{2g} levels and empty e_g states (LS, $t_{2g}^6 e_g^0$, $S = 0$). At ≈ 100 K $LaCoO_3$ undergoes a
transition to a magnetic state, the character of which is still under question. Possible states of
the Co^{3+} ion that can give rise to the magnetism correspond either to the intermediate spin (IS,
$t_{2g}^5 e_g^1$, $S = 1$) or to the high spin (HS, $t_{2g}^4 e_g^2$, $S = 2$) states.

LaCoO$_3$ crystallizes in a rhombohedral space group $R\bar{3}c$. The structure description involves three parameters: lattice constant a, rhombohedral angle α and oxygen coordinate x. These three parameters could also be expressed in terms of the Co–O–Co bond angle β and the geometry of the CoO$_6$ octahedron: the Co–O bond length d and the trigonal distortion characterized by the O–Co–O angle γ. The dependence of the crystal structure on temperature was studied by neutron diffraction in [1, 2]. No deviation from the $R\bar{3}c$ symmetry induced by the magnetic transitions was found in these papers. Recently, however, a monoclinic distortion of the structure (space group $I2/a$) over the temperature range 100–300 K was suggested based on a single-crystal x-ray diffraction study [3].

Interpretation of the temperature induced magnetic transition by an *ab initio* calculation of the electronic structure is complicated by two problems. First, the density functional theory (DFT), on which such calculations are usually based, only concerns the 0 K ground state. Second, there is strong correlation of the electrons of the magnetic cations in the 3d magnetic oxides. The two methods which are usually applied in the DFT based calculations, the local density approximation (LDA) or the generalized gradient approximation (GGA), often fail to describe correctly systems with strong correlation.

A possible way to overcome the above two problems was suggested by Korotin *et al* [4]. These authors assumed that the spin-state transition in LaCoO$_3$ is driven by the change of the crystal structure with temperature, i.e. the entropy part of the free energy was neglected. The temperature evolution of the electronic structure have been obtained by adopting the crystal structure determined experimentally at different temperatures [1] and performing the corresponding series of *ab initio* calculations. To account for the strong electron correlations of the 3d electrons of cobalt, the LDA + U approach was used [5, 6]. In LDA + U-like methods an orbitally dependent potential is introduced for the chosen set of electron states, which in this case are the 3d states of Co. The method is no longer truly *ab initio* as the values of the Hubbard parameter U and the exchange parameter J must be inserted ($U = 7.8$ eV and $J = 0.92$ eV were used in the paper of Korotin *et al* [4]).

In order to determine the energy differences between the LS, IS and HS states, Korotin *et al* employed the fixed-spin-moment (FSM) method. In this method the total energy of the system is minimized under the condition that the total spin moment is fixed at a prescribed value. In agreement with the experiment the ground state was found to be LS for the low temperature structures. The total energy per formula unit of the IS and HS states were higher by 0.24 and 0.65 eV, respectively. With increasing temperature, the energies of IS and LS states crossed at $\sim$150 K and the IS state became the ground state for higher temperatures. The energy of the HS state was the highest over the whole temperature range.

Similar results were later obtained in [7], where the electronic structure of the rhombohedral LaCoO$_3$ perovskite was calculated for a number of structures with varying CoO$_6$ octahedra geometry by the GGA + U method. These calculations were carried out without fixing the spin moments. For each structure the GGA calculation was performed first and then the GGA + U calculation was started using the electron density and occupation matrices of the converged GGA. The IS state was found to be more stable than the LS state for structures with longer Co–O length and more open Co–O–Co angle. The GGA + U results were also in agreement with the observed pressure induced IS–LS transition [8].

The calculation of the electronic structure of the La$_{1-x}$Sr$_x$CoO$_3$ system using the GGA without the Hubbard U correction was reported by Ravindran *et al* [9]. For $x = 0$ the crystal structure corresponding to 4 K was considered, and it was found that the LS state has the lowest energy. Using the FSM method the energy of the IS and HS states were found to be higher by 0.025 and 1.124 eV, respectively.

The DFT calculations described above supposed a homogeneous state of one type of Co^{3+} species, since the experimentally determined $R\bar{3}c$ space group only allows a single crystallographically independent Co site. Using the model Hamiltonian, Zhuang *et al* [10] pointed out that if the symmetry is formally lowered to allow for two or more crystallographically independent Co sites, an inhomogeneous solution can be stabilized. They examined magnetically ordered states of an enlarged double cell with all possible combinations of LS, IS and HS states, including both ferro- and antiferromagnetic (AF) ordering within the unrestricted Hartree–Fock method. *They found a mixture of LS and HS states to be lower in energy than the uniform IS state.*

The $R\bar{3}c$ cell in a rhombohedral setting (primitive cell) contains two formula units of LaCoO$_3$, i.e. two Co sites, which are crystallographically equivalent. A straightforward way of creating two independent Co sites with different spin states is by lowering the symmetry from $R\bar{3}c$ to $R\bar{3}$. Then, in addition to three homogenous solutions, LS, IS and HS, three ferromagnetically aligned combinations of different spins, LS–IS, LS–HS and IS–HS, and three antiferromagnetically aligned combinations of spins, IS–IS–AF, HS–HS–AF and IS–HS–AF, are possible. In total, $R\bar{3}$ symmetry with two independent Co sites allows nine combinations of spin states, as considered in [10]. The important feature of the structure with $R\bar{3}$ symmetry is that one kind of Co site is only surrounded by the other kinds of Co sites. This means, for example for LS–HS spin-state combinations, that all six nearest neighbours of Co in the HS state are in the LS state and vice versa. This kind of magnetic phase was also proposed for LaCoO$_3$ by Señarís-Rodríguez and Goodenough [11]. When calculating the relative energies of the different spin states it is necessary to take into account that the atomic radii of LS, IS and HS Co^{3+} ions are different [2]. The GGA $+ U$ calculations presented in this paper show that, provided the lengths of the Co–O–Co bonds are optimized, the LS–HS state is the nearest excited state at 0 K, lying only $\approx$25 meV above the homogeneous LS ground state. As the temperature is raised the energy of the LS–HS state with Co$_{LS}$–O–Co$_{HS}$ bond optimization decreases and above $\approx$200 K it intersects the energy of the LS state. Supported by present calculations, the previously published experiments on the paramagnetic susceptibility and thermal expansion [12] are analyzed and consistently interpreted within the LS–HS scenario.

2. Method of calculation

The calculations were made with the WIEN2k program [13]. This program is based on the DFT and uses the full-potential linearized augmented plane wave (FP LAPW) method with the dual basis set. In LAPW methods the space is divided into atomic spheres and the interstitial region. The electron states are then classified as the core states, that are fully contained in the atomic spheres, and the valence states. The valence states are expanded using the basis functions; each of the basis function has the form of the plane wave in the interstitial region, while it is an atomic-like function in the atomic spheres. To make possible the treatment of two valence functions with the same orbital number (like 3p and 4p functions of Co) so-called local orbitals are added to the basis functions [14]. In our calculations the electronic configuration of the core states corresponded to (Ne, 3s^2) for Co, to (He) for O and to (Kr, 4d^{10}) for La atoms. The number n_k of the k points in the irreducible part of the Brillouin zone was 85 and the number n_b of the basis functions was $\approx$100 per atom in the unit cell (n_b differs somewhat for different k points). All calculations were spin-polarized. For the exchange correlation potential we adopted the GGA form [15]. The radii of the atomic spheres were 2.30, 1.90 and 1.60 au for La, Co and O, respectively. To improve the description of Co 3d electrons we used the GGA $+ U$ method, which corresponds to the LDA $+ U$ method described in [5, 6] with the GGA correlation potential instead of LDA.

In the LDA + U-like methods an orbitally dependent potential is introduced for the chosen set of electron states, which in our case are 3d states of Co. The additional potential has an atomic Hartree–Fock form, but with screened Coulomb and exchange interaction parameters. The problem is that the exchange and correlation already contained in the LDA or GGA should be subtracted. The form of this 'double counting correction' is spherically symmetrical, and it is not clear to what extent its application in the full potential methods is justified, as there is no 'double counting correction' for the non-spherical terms in the GGA + U orbital potential. We avoided this problem by using effective $U_{\text{eff}} = U - J$ instead of the parameter U and putting the non-spherical terms in orbital potential equal to zero. Thus the notation $U \equiv U_{\text{eff}}$ is used, but it should be kept in mind that we are dealing with the effective U which is smaller than the Hubbard parameter.

The self-consistent procedure that uses LSDA or GGA often yields different solutions (e.g. ferromagnetic and antiferromagnetic) for different initial spin densities. This feature is even more pronounced in the LDA + U (GGA + U) methods where multiple solutions may often be stabilized when the calculation is started with different occupations of the orbital states to which LDA + U is applied. Using this fact the total energies of various spin configurations, described in section 3, were obtained.

3. Results

The lattice parameters and atomic positions were taken from [2], namely parameters for structures determined at $T = 5, 300, 450$ and 800 K. The experimental symmetry $R\bar{3}c$ was lowered to $R\bar{3}$ to create two independent Co sites. The DFT calculations were performed for three different values of $U = 2.7, 3.5$ and 4.5 eV. They gave qualitatively similar results, so in the following text we will focus on the results obtained with $U = 2.7$ eV.

The GGA + U calculation, without using the FSM method, converged for the following six spin combinations: LS, IS, LS–IS, LS–HS, IS–IS–AF and HS–HS–AF. It was only possible to converge the HS state using the FSM method. It was not possible to stabilize the remaining two spin combinations, IS–HS and IS–HS–AF, as they converged during the iteration process to solutions identical to IS–IS and HS–HS–AF, respectively.

The dependence of the relative energy of various spin-state combinations on the temperature is displayed in figure 1. The ground state at 5 K is the LS state, in agreement with experimental observation. The two nearest spin states in energy are the LS–HS and IS states, which are 60 and 73 meV higher, respectively. The LS–IS state is 106 meV above the LS state. The most stable antiferromagnetic state is HS–HS–AF, which is 228 meV higher than the LS state. The energies of the IS–IS–AF and HS states, which are not displayed, are more than 500 and 700 meV, respectively, above the ground LS state.

For the IS state the ferromagnetic configuration is 500 meV lower in energy than the corresponding antiferromagnetic IS–IS–AF state. On the other hand, the HS–HS–AF state is about 500 meV more stable than the corresponding HS ferromagnetic state. This is in agreement with theoretical predictions [16, 17]—ferromagnetic interaction is expected between Co with a $t_{2g}^5 e_g^1$ configuration, whereas for Co with a $t_{2g}^4 e_g^2$ configuration antiferromagnetic interaction is predicted.

The energy dependence of LS–HS and IS states on the temperature is very similar, both are stabilized with increasing temperature (i.e. increasing cell volume). The energy of the IS state is decreasing slightly faster, so LS–HS and IS cross around 400 K, and at high temperature the energy of the IS state is lower. The LS state is destabilized with increasing temperature. The LS state crosses IS and LS–HS at approximately the same temperature, 450 K. The energy of the LS–IS state is 70–110 meV above the ground state for all temperatures. The stabilization
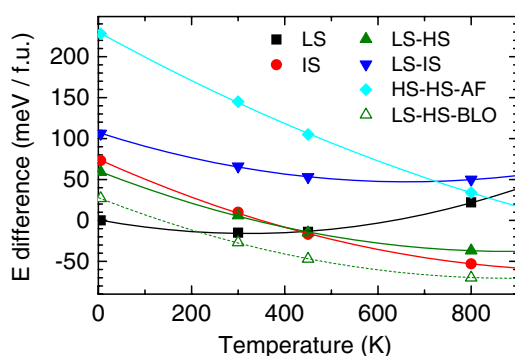
Figure 1. The dependence of relative energy per formula unit LaCoO₃ on temperature for the spin-state combinations LS, IS, LS–HS, LS–IS, HS–HS–AF and for the LS–HS–BLO state including Co$_{LS}$–O–Co$_{HS}$ bond length optimization (Co–O bond length difference = 0.06 Å).
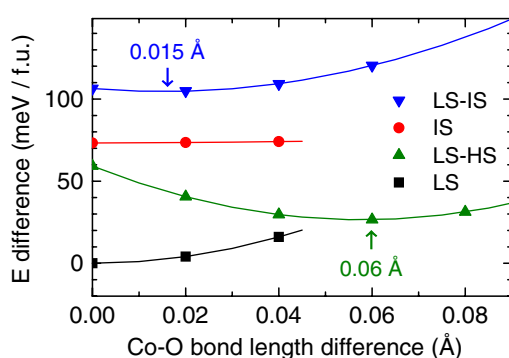

Figure 2. The dependence of relative energy on Co size difference for spin-state combinations LS, IS, LS–HS and LS–IS for structures at 5 K.

of HS–HS–AF with increasing temperature is the fastest of the displayed spin states, but still it remains above the ground state over the whole calculated temperature range.

The ionic radius of Co³⁺ depends on the Co spin state, namely it increases from r_{LS} = 0.545 Å to r_{IS} = 0.56 Å and r_{HS} = 0.61 Å [2]. Therefore, further stabilization of the mixed spin states could be expected if the structure is relaxed to allow different sizes for the two Co sites.

The dependence of various combinations of spin states on the Co size difference is displayed in figure 2 for structures at 5 K. The LS–HS state is significantly stabilized by Co size optimization. It is interesting that the minimum energy is for a Co size difference of 0.06 Å, i.e. the expected difference between ionic radii of Co³⁺ in the HS and LS states [18]. The LS–IS state is only slightly stabilized and the minimum energy also corresponds to the expected difference between the ionic radii of Co³⁺ in IS and LS states, 0.015 Å [2]. The energy of the IS state does not change with increasing size difference of the Co sites and the LS state is even destabilized.

The LS–HS state with Co–O bond length optimization, i.e. LS–HS–BLO, is more stable than IS over the whole temperature range (see figure 1). The energy of the LS and LS–HS–BLO states crosses around 200 K.

Figure 3 shows the total density of states (DOS) of LaCoO₃ in LS, LS–HS, IS and LS–IS states at 5 K. The LS and LS–HS states are insulators with a gap of 0.75 and 0.45 eV,
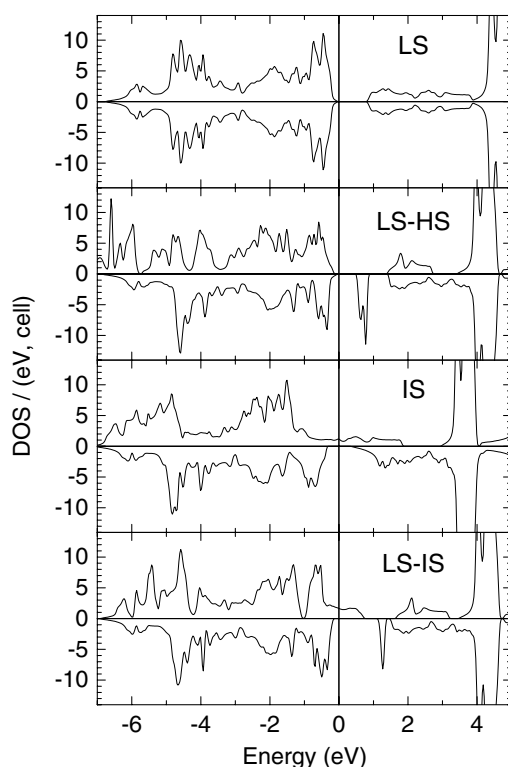
Figure 3. Total DOS for LS, LS–HS, IS and LS–IS spin states.

Table 1. Occupation of t_{2g} and e_g orbitals, charge and magnetic moments in μ_B of Co calculated for 5 K structures.

	LS		LS–HS		IS		LS–IS		HS–HS–AF		LS–HS–BLO	
	t_{2g}	e_g	t_{2g}	e_g	t_{2g}	e_g	t_{2g}	e_g	t_{2g}	e_g	t_{2g}	e_g
IS or HS ↑	—	—	2.78	1.86	2.74	1.47	2.75	1.37	2.76	1.86	2.77	1.87
IS or HS ↓	—	—	1.24	0.50	1.78	0.49	1.86	0.52	1.15	0.62	1.25	0.48
LS ↑	2.66	0.62	2.71	0.78	—	—	2.69	0.78	—	—	2.71	0.73
LS ↓	2.66	0.62	2.59	0.49	—	—	2.60	0.52	—	—	2.60	0.52
	Charge	μ_B	Charge	μ_B	Charge	μ_B	Charge	μ_B	Charge	μ_B	Charge	μ_B
IS or HS	—	—	2.24	2.91	2.16	1.96	2.15	1.75	2.22	2.86	2.27	2.93
LS	2.09	0.00	2.08	0.42	—	—	2.07	0.35	—	—	2.05	0.34

respectively. The IS and LS–IS states are half-metals. The occupation of t_{2g} and e_g orbitals, charge and magnetic moments of Co calculated for structures at 5 K are summarized in table 1.

The DOS of the LS state is displayed in figure 4. The states just below E_F correspond to Co(t_{2g}) and O(p) states, whereas the states just above the Fermi level are of Co(e_g) character.

The DOS of the LS–HS state is displayed in figure 5. The states below the Fermi level are mostly contributed by the t_{2g} bands of Co in the LS state and O(p) bands. A sharp peak above the Fermi level belongs to the Co-HS(t_{2g}) band. The total magnetic moment per unit cell is exactly 4 μ_B (the unit cell contains two formula units of LaCoO₃). The integer value of
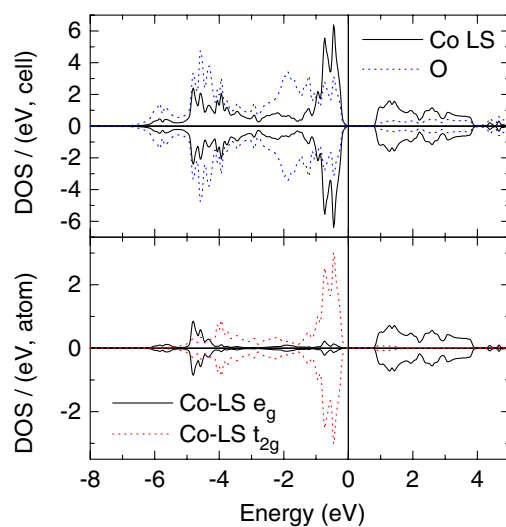
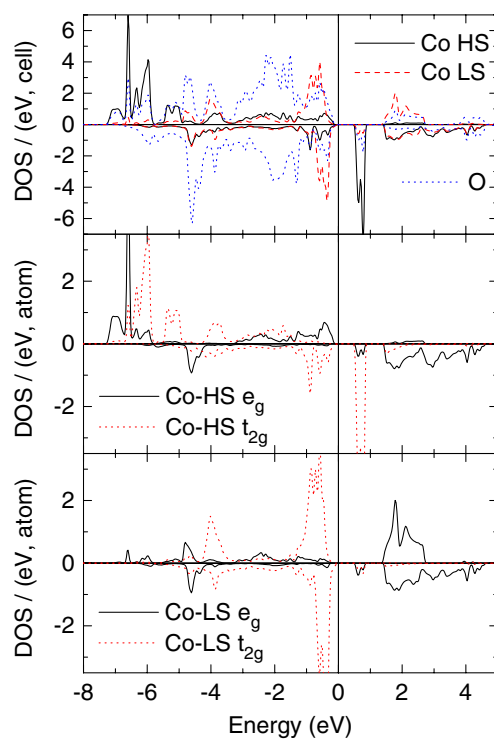**Figure 4.** DOS of Co and O for the LS state.

Figure 5. DOS of Co and O for the LS–HS state.

magnetic moment is to be expected for a system with an energy gap in at least one of the spin channels [7]. Due to hybridization, the magnetic moments on individual Co ions differ from the ideal values of 4 and 0 μ_B expected for HS and LS, respectively (see table 1). The DOS is not significantly changed by Co size optimization.
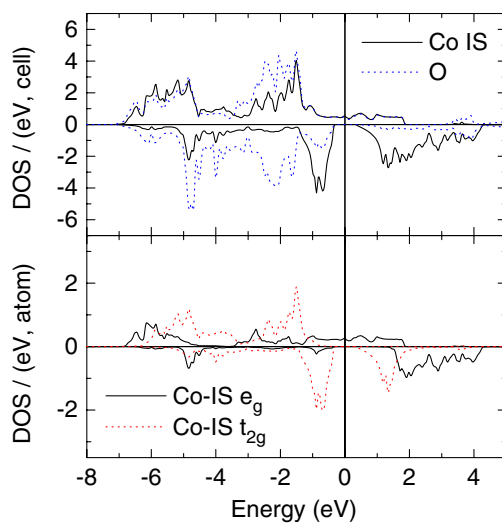
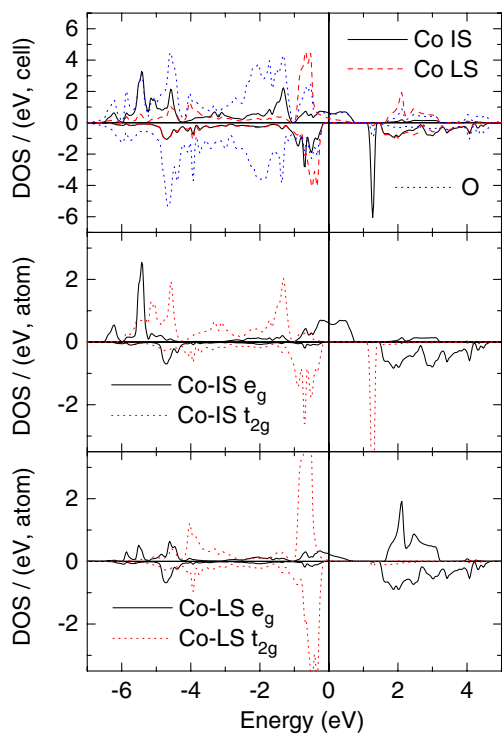**Figure 6.** DOS of Co and O for the IS state.

Figure 7. DOS of Co and O for the LS–IS state.

The DOS of the IS state is displayed in figure 6. The DOS has a half-metal character with conduction in the majority spin channel only. The states on E_F are Co(e_g) strongly hybridized with the O p states. The total magnetic moment per unit cell is 4 μ_B.

The DOS of the LS–IS state is displayed in figure 7. The DOS has half-metal character similar to the DOS of the IS state. The states on E_F are mixed Co-IS(e_g) and O(p) bands with a
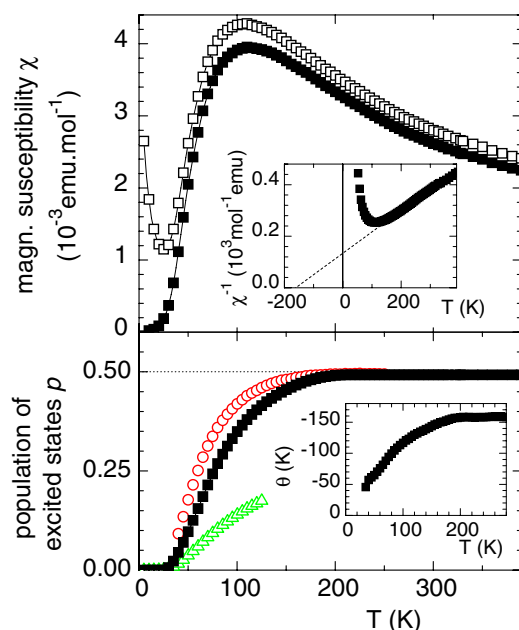
Figure 8. Analysis of LaCoO$_3$ magnetic susceptibility considering Co in the LS–HS state. Upper panel: raw susceptibility (open symbol) and corrected data (full symbols). The inset shows inverse susceptibility. Lower panel: population of excited states p calculated from equation (1) ($\triangle$), from equation (2) with fixed $\theta = -160$ ($\bigcirc$), and a more realistic variant with variable θ ($\blacksquare$), calculated to fit the CoO$_6$ octahedra expansion data [2]. The inset show the derived dependence of θ on temperature.

small contribution of Co-LS(e$_g$). A sharp peak above the Fermi level belongs to the Co-IS(t$_{2g}$) band. The total magnetic moment per unit cell is 2 μ_B.

Different Co spin states exhibits slightly different charges. The calculated charges of Co in the LS, IS and HS states are around +2.08, +2.16 and +2.24, respectively (see table 1). The charges deviate from theoretical value of +3 due to the hybridization.

4. Discussion

The presented GGA + U results indicate that the nearest excited state of Co^{3+} in LaCoO$_3$ is HS, provided that the neighbouring sites are in the LS state. Antiferromagnetic interactions may be expected between next-nearest Co ions in HS states, since they are separated by diamagnetic Co in the LS state. Thus the saturated state at the middle temperature range is possibly an ordered array of the size-differentiated LS and HS sites, the LS–HS–LS–HS–AF combination. However, detailed investigation of this spin combination, involving various AF spin arrangements in cells with at least four independent Co sites, is outside the scope of this paper. It is worth mentioning that the observed Co size difference of 0.06 Å is comparable with normal thermal fluctuations, suggesting that the origin of the saturated LS + HS(1:1) phase can be regarded as a freezing of a soft high-temperature mode that couples breathing lattice phonons with an electronic mode consisting of the NaCl-type LS/HS correlations. Below $\approx$100 K, the ordering is melted and a homogeneous LS phase is stabilized progressively.

The temperature evolution of LaCoO$_3$ is evidenced in the magnetic and dilatometric measurements. The susceptibility data in figure 8 are taken from [12]. After the subtraction

of the temperature independent diamagnetic contribution and the paramagnetic Van Vleck susceptibility (in total 10^{-4} emu mol^{-1}), and a small Curie-like term due to impurity, observed at the lowest temperatures only, the corrected susceptibility curve demonstrates a rapid population of the paramagnetic Co^{3+} species in the $LaCoO_3$ ground state, which takes place between 50 and 100 K. Above 150 K, the inverse susceptibility (see inset to the upper panel of figure 8) shows a linear Curie–Weiss behaviour, suggesting that the magnetic transition is saturated, the effective magnetic moments are temperature independent at least over the 150–350 K range and the prevailing interactions are of the anticipated AF type.

The susceptibility in $LaCoO_3$ has usually been analysed in terms of statistically independent excitations from a ground low spin state to either IS or HS states, neglecting the magnetic interactions and considering spin-only values for moments of the Co^{3+} species [12, 19–21]. However, the real situation is more complex due to partial occupation of the t_{2g} levels allowing appreciable orbital momentum. Our results in the middle panel of figure 5 clearly show that electrons in the LS–HS phase are localized and obviously of the $t_{2g}^4 e_g^2$ configuration. Magnetism in that case is governed by multiplets originating from the $^5T_{2g}$ ionic term in the crystal field of oxygen ligands. Actually, the term is split by the spin–orbit coupling to a triplet, quintet and septet (see, e.g., p. 443 in [22]). According to recent effective Hamiltonian calculations of Ropka and Radwanski [23] and the ESR experiments of Noguchi *et al* [24], the lowest-lying spin–orbit triplet (fictitious $\tilde{J} = 1$) of the HS origin is situated in $LaCoO_3$ a mere 140 K above the LS singlet, and corresponds to an effective $g_{\tilde{J}} = 3.35$. Higher spin–orbit multiplets (quintet and septet) are far off in energy and their effects can be neglected, at least below 100 K. Considering an HS impurity model at low temperatures, the corrected susceptibility can be directly related to the population of excited Co^{3+} states $p(T)$ by the expression

$$\chi(T) = \frac{N_A \mu_B^2}{3k_B T} \mu_{eff}^2 p(T) \tag{1}$$

where N_A is the Avogadro number, μ_B the Bohr magneton, k_B the Boltzmann constant and $\mu_{eff} = g_{\tilde{J}} \sqrt{\tilde{J}(\tilde{J}+1)} = 4.74$ is the effective moment, relevant to the triplet. There is some peculiarity that an identical result is obtained when considering for the HS species the spin-only moment $\mu_{eff} = g\sqrt{S(S+1)}$ and $g = 1.95$.

The population of excited states $p(T)$ calculated from equation (1) using the corrected $\chi(T)$ is shown in the lower panel of figure 8 as triangular symbols. It is seen that the derived population does not tend to the saturation ($p = 0.5$) above 150 K as suggested by the inverse susceptibility, which means that the isolated HS impurity model is applicable only up to about 50–60 K where the HS fraction does not exceeds 5%. As the population of excited states p increases further, the AF next-nearest HS–LS–HS interactions become effective. The susceptibility is given by a Curie–Weiss dependence

$$\chi(T) = \frac{N_A \mu_B^2}{3k_B (T - \theta)} \mu_{eff}^2 p(T) \tag{2}$$

where the parameter θ approaches -160 K (see the inset in the upper panel of figure 8). The population of excited states p, shown as circles in the lower panel of figure 8, was calculated using $\mu_{eff} = 4.40$ in order to fit the saturation value $p = 0.5$. As argued in the conclusions, we relate this temperature independent moment to the spin-only multiplet $S = 2$ with $g = 1.8$. The reduced value of g is in agreement with the hybridization effects in our electron structure calculations.

Finally, in a more realistic model, the parameter θ was allowed to decrease with decreasing temperature and HS population. The dependence displayed in the inset in the lower panel

of figure 8 was obtained in the fit with the anomalous expansion of CoO_6 octahedra (see, e.g., [12, 20, 21]). The experimental data used in the present analysis are not based on the lattice dilatation but on a direct measurement of Co–O bond length, using the neutron diffraction experiments of Radaelli *et al* [2]. The anomalous expansion in $LaCoO_3$ comes from the larger size of the HS Co^{3+} ion compared to LS, and is thus in first approximation proportional to the HS population. As concerns the linear expansion coefficient, one easily obtains the relation

$$\alpha_{anom} = \frac{dp}{dT}d \tag{3}$$

where d is the relative change of the average Co–O bond length between LS and HS states. Its actual value is difficult to guess, also because of the fact that LS and HS sites within one structure are subjected to an opposite internal stress. To achieve the saturation at $p = 0.5$, d should be taken as 0.0037. This corresponds to the difference in Co^{3+} radii of 0.007 Å, which is a very small difference compared to the tabulated values of ionic radii ($r_{LS} = 0.545$ Å, $r_{HS} = 0.610$ Å). This may point to the dynamic nature of the LS–HS correlations, even in the saturated LS + HS(1:1) phase (see also the arguments of Señarís-Rodríguez and Goodenough [11]).

In summary, consistent analysis of the susceptibility and dilatometric experiments within the LS–HS scenario gives the HS population shown by full squares in the lower panel of figure 8. The AF interactions of growing strength, manifested by the temperature dependent parameter θ in Curie–Weiss law, become evident starting from about 40 K (see the inset). The effective moments associated with the HS Co^{3+} species vary slightly from the value $\mu_{eff} = 4.74$ for the impurity states at low temperatures to about $\mu_{eff} = 4.40$ for the LS + HS(1:1) phase over the 150–350 K range. Our results can be related to the HS–LS energy difference. Taking into account that the HS state is only stabilized if it is surrounded by six LS, the population of excited states p is given by the expression

$$\frac{p}{(1-p)} = (1-p)^6 \nu e^{-E/T} \tag{4}$$

where ν is the degeneracy of HS states in the paramagnetic phase, which vary from $2\tilde{J}+1 = 3$ at the first stages of the magnetic transition to $2S + 1 = 5$ when the LS + HS(1:1) phase is saturated, and E is the required energy difference in units of T. The calculation shows that $E = 180$ K (16 meV) at the lowest temperature, which is comparable with the calculated energy difference between LS and LS–HS–BLO states (25 meV). With increasing HS population, starting at about 40 K, the energy difference is rapidly reduced. The HS–LS crossover takes place at 100 K where the LS → LS + HS transition is 70% completed. The diamagnetic–paramagnetic transition in $LaCoO_3$ thus starts as thermal excitations but at final stages it acquires a character of a regular phase transition, where cooperative action of larger HS Co^{3+} ions on the lattice expansion results in a stabilization of the LS + HS(1:1) phase.

The $R\bar{3}$ symmetry used in our calculation does not allow Jahn–Teller deformation of CoO_6 octahedra. It may be expected that cooperative Jahn–Teller deformation, allowing optical-mode displacement of the oxygen atoms to give long Co–O bonds with occupied e_g orbitals coupled to short Co–O bonds with empty e_g orbitals on the opposite side, lowers the energy of the IS state. However, our preliminary calculations for structures with lower symmetry than $R\bar{3}$ showed that any structure with a deformation of CoO_6 octahedra greater than 0.01 Å (the difference between the Co–O bond lengths) has a higher energy than the ideal rhombohedral one. Calculation in low symmetry cells with at least four independent Co sites, involving the LS–HS–LS–HS–AF spin arrangements mentioned at the beginning of the discussion, will be a subject of further study.

5. Conclusions

GGA $+ U$ calculations for $LaCoO_3$ confirm the existence of a stationary state composed of a mixture of LS and HS Co^{3+} ions in a 1:1 ratio, which is of insulating character. At the lowest temperatures, this state is located at an energy about 60 meV above the homogeneous LS ground state. This energy difference is reduced to 25 meV if Co_{LS}–O–Co_{HS} bond length optimization is applied. The energy difference decreases with the lattice dilatation and the LS $+$ HS(1:1) phase becomes stable at some intermediate temperature. These results, together with previous ESR evidence for HS excitations in the LS ground state, lead to the conclusion that the diamagnetic–paramagnetic transition in $LaCoO_3$ at 50–150 K is caused by a gradual population of HS Co^{3+} ionic states, conditioned by exclusion of HS–HS nearest neighbours. Analysis of the paramagnetic susceptibility data within this LS–HS scenario shows the presence of the AF interactions HS–LS–HS, starting at about 40 K and becoming more effective with increasing HS population. Finally, the LS $+$ HS(1:1) phase is saturated above 150 K and the susceptibility acquires a simple Curie–Weiss behaviour in which AF interactions are characterized by the parameter $\theta = -160$ K. Anomalous expansion data suggest that LS–HS correlations are probably of dynamic character, even in the saturated phase.

   The susceptibility data show that at the first stages of magnetic transition the HS species form impurity states where the spin–orbit coupling plays an important role. The effective moments of HS in the temperature range up to 100 K are determined by the magnetic properties of the low-lying triplet and amount to ($\mu_{eff} = 4.74$). At higher temperatures, a quasi-linear decrease of μ_{eff} can be anticipated (to about 4.3 at 350 K) due to thermal population of the higher-lying quintet and septet. Experiment shows, instead, that the moments are constant in a relatively broad temperature range 150–350 K and amount to $\mu_{eff} = 4.40$. This makes the scheme of spin–orbit multiplets questionable and suggests that orbital momenta in $LaCoO_3$ are effectively cancelled or strongly reduced at intermediate temperatures. Two factors might be responsible—formation of molecular orbitals upon the growth of LS–HS ordered regions and the effects of finite temperature. Our trial calculations by WIEN2k including the spin–orbit coupling showed, indeed, that the orbital component is about 0.15 μ_B at maximum. This result refers, however, to the magnetically ordered phase while $LaCoO_3$ is in a paramagnetic state, which should lead to a finite-time localization and onset of spin–orbit coupling. Therefore, we relate the vanishing orbital momenta to lattice fluctuations that act primarily on bonding and, therefore, on orbitals. This decouples the spin and orbital dynamics (the spin and orbital lifetimes are different) leading to the essentially spin-only values of observed effective moments.

Acknowledgments

References

[1] Thornton G, Tofield B C and Hewat A W 1986 *J. Solid State Chem.* **61** 301
[2] Radaelli P G and Cheong S-W 2002 *Phys. Rev.* B **66** 094408
[3] Maris G, Ren Y, Volotchaev V, Zobel C, Lorenz T and Palstra T T M 2003 *Phys. Rev.* B **67** 224423
[4] Korotin M A, Ezhov S Y, Solovyev I V, Anisimov V I, Khomskii D I and Sawatzky G A 1996 *Phys. Rev.* B **54** 5309

[5] Anisimov V I, Solovyev I V, Korotin M A, Czyzyk M T and Sawatzky G A 1993 *Phys. Rev.* B **48** 16929
[6] Liechtenstein A I, Anisimov V I and Zaanen J 1995 *Phys. Rev.* B **52** R5467
[7] Knížek K, Novák P and Jirák Z 2005 *Phys. Rev.* B **71** 054420
[8] Vogt T, Hriljac J A, Hyatt N C and Woodward P 2003 *Phys. Rev.* B **67** 140401(R)
[9] Ravindran P, Fjellvåg H, Kjekshus A, Blaha P, Schwarz K and Luitz J 2002 *J. Appl. Phys.* **91** 291
[10] Zhuang M, Zhang W and Ming N 1998 *Phys. Rev.* B **57** 10705
[11] Señarís-Rodríguez M A and Goodenough J B 1995 *J. Solid-State Chem.* **116** 224
[12] Knížek K, Jirák Z, Hejtmánek J, Veverka M, Maryško M, Maris G and Palstra T T M 2005 *Eur. Phys. J.* B **47** 213
[13] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Techn. Universtät Wien Austria) (ISBN 3-9501031-1-2) version 2005
[14] Singh D 1994 *Plane Waves, Pseudopotentials and the LAPW Method* (Dordrecht: Kluwer–Academic)
[15] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[16] Goodenough J B 1955 *Phys. Rev.* **100** 564
[17] Kanamori J 1959 *J. Phys. Chem. Solids* **10** 87
[18] Shannon R D 1976 *Acta Crystallogr.* A **32** 751
[19] Yan J-Q, Zhou J-S and Goodenough J B 2004 *Phys. Rev.* B **69** 134409
[20] Zobel C, Kriener M, Bruns D, Baier J, Grüninger M, Lorenz T, Reutler P and Revcolevschi A 2002 *Phys. Rev.* B **66** 020402(R)
[21] Baier J, Jodlauk S, Kriener M, Reichl A, Zobel C, Kierspel H, Freimuth A and Lorenz T 2005 *Phys. Rev.* B **71** 14443
[22] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon)
[23] Ropka Z and Radwanski R J 2003 *Phys. Rev.* B **67** 172401
[24] Noguchi S, Kawamata S, Okuda K, Nojiri H and Motokawa M 2002 *Phys. Rev.* B **66** 94404