Stabilization of the high-spin state of Co\(^{3+}\) in LaCo\(_{1-x}\)Rh\(_x\)O\(_3\).  

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The rhodium doping in the LaCo\(_{1-x}\)Rh\(_x\)O\(_3\) perovskite series (\(x = 0.02 - 0.5\)) has been studied by X-ray diffraction, electric transport and magnetization measurements, complemented by electronic structure GGA+U calculations in supercell for different concentration regimes. No charge transfer between Co\(^{3+}\) and Rh\(^{3+}\) is evidenced. The diamagnetic ground state of LaCoO\(_3\), based on Co\(^{3+}\) in low-spin (LS) state, is disturbed even by a small doping of Rh. The driving force is the elastic energy connected with incorporation of a large Rh\(^{3+}\) cation into the matrix of small LS Co\(^{3+}\) cations, which is relaxed by formation of large Co\(^{3+}\) in high-spin (HS) state in the next-nearest sites to the inserted Rh atom. With increasing temperature, the population of Co\(^{3+}\) in HS state increases through thermal excitation, and a saturated phase is obtained close to room temperature, consisting of a nearest-neighbor correlation of small (LS Co\(^{3+}\)) and large (HS Co\(^{3+}\) and LS Rh\(^{3+}\)) cations in a kind of double perovskite structure. The stabilizing role of elastic and electronic energy contributions is demonstrated in supercell calculations for dilute Rh concentration compared to other dopants with various trivalent ionic radius.

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I. INTRODUCTION

The cobalt perovskites LnCoO\(_3\) (\(Ln = \text{La, Y, rare-earths}\)) show various anomalous behaviors that are associated with changes of the spin state of octahedrally coordinated Co\(^{3+}\) ions of 3\(d^9\) configuration. According to recent interpretation in the frame of LS-LS/HS-IS model, the process can be understood as a local excitation of Co\(^{3+}\) ions from the diamagnetic LS (low spin, \(t_{2g}^6\)) ground state to closely lying paramagnetic HS (high spin, \(t_{2g}^5e_{g}^1\) states, followed at higher temperature by a formation of a metallic-like phase of IS character (intermediate spin, \(t_{2g}^5\sigma^*\)) - see e.g. [1,2]. In LaCoO\(_3\) these two steps are well separated (\(T_{\text{magn}} = 70\) K, \(T_{\text{I-M}} = 535\) K). The experiments show that the HS population, after a steep increase at \(T_{\text{magn}}\), tends quickly to a saturation, reaching 40-50% in maximum - see e.g. the combined analysis of susceptibility and anomalous expansion data in [4]. To account for such behavior, two formal approaches have been used. In the first one, Kyönen et al. treat the excitations as locally independent events obeying Boltzmann statistics and relate the actual course of the diamagnetic-paramagnetic transition to lattice effects. An activation energy increasing progressively with HS population is obtained [1]. An alternative approach is based on original idea of Goodenough that the stabilization of HS state is conditioned by presence of LS states in the neighborhood. As shown by Knížek et al. [3] using a simple probabilistic model, when nearest HS neighbors are forbidden, the activation energy found by the fit has an opposite trend - it decreases with temperature (or equivalently with HS population) leading finally to a crossover. Such behavior finds a strong support in GGA+U calculations [3] and also the limiting HS population of about 45% can be naturally explained.

An uncertainty exists also concerning the formation of metallic phase at around 535 K. The gradual course of this process, which is in striking contrast with standard I-M transition, has been modeled as a thermal excitation to IS states [4]. However, it is worth mentioning that the two-step transitions in LaCoO\(_3\) does not necessarily require an existence of three close lying ionic configurations (LS, HS and IS). A reference can be done to phenomenological model of Bari and Sivardièere, who investigated the activation from the LS ground state to excited HS states including the magnetoelastic coupling between the two species [4]. Depending on the model parameters, they obtained a succession of three phases in coherence with experimental findings - the mixed LS/HS states with gradually increasing HS weight at low temperatures, the disproportionation of HS-poor and HS-rich sites in the intermediate range, and a re-entered homogeneous phase of LS/HS admixed states at high temperatures. Very recently this scenario of spin-state transitions in LaCoO\(_3\) based on two states only was supported in a study of a two-orbital Hubbard model with crystal-field splitting using DMFT calculation by Kuneš and Krápek [5]. They demonstrated that the existence of disproportionated phase and subsequent homogenization combined with closing of the charge gap can be understood considering the on-site interactions of valence electrons and their itinerancy. This suggests that the physics of LaCoO\(_3\) is primarily of electronic (fermionic) origin, and elastic interactions between different spin-state species have just a stabilizing effect.

The present study is undertaken with an aim to resolve by experimental and theoretical means the role of electronic and elastic interactions in the stabilization of
various Co$^{3+}$ spin states in the LaCoO$_3$ type related systems, in particular in LaCoO$_3$-LaRhO$_3$ solutions. The studies on Rh-containing compounds were not frequent in the past, mainly due to high cost of rhodium, which limits potential applications. Nevertheless, since Rh$^{3+}$ of 4$d^6$ configuration is isoelectronic with Co$^{3+}$ as regards the valence electrons, and is exclusively in low-spin state, the substitution is helpful in the fundamental research of cobalt spin states and experienced an increased interest in the last years. Complete LaCo$_{1-x}$Rh$_x$O$_3$ solid solution was recently studied in Ref. [3] with focus on transport properties at high temperature and in Ref. [4] with focus on magnetic properties. Influence of small Rh doping on the spin state transition in LaCoO$_3$ was presented in [10].

Our work revisits this system, focusing to compositions with small doping of Rh ($x = 0 - 0.08$), including for completeness also the $x = 0.2$ and 0.5 samples. The experiments are complemented with GGA+U electronic structure calculations using the supercell with regular orderings of Co and Rh ions corresponding to doping $x = 1/16 = 0.0625$, $1/2$ and $15/16 = 0.9375$. The method applied allows us to investigate not only various valence and spin states in the model structures but also to optimize local bond lengths and angles that stabilize the given configuration. The role of temperature is simulated by a change of unit cell volume. In agreement with the experimental findings, the calculations support the significant HS populations preserved in the LaCo$_{1-x}$Rh$_x$O$_3$ systems down to the lowest temperature, and suggest that the stabilization of HS Co$^{3+}$ states compared to undoped LaCoO$_3$ is to much extent due to elastic interactions. Namely, the low-energy configurations are based on a nearest neighbor correlations of Co$^{3+}$ states of smaller size and HS Co$^{3+}$ or LS Rh$^{3+}$ states of larger size in a kind of the double perovskite $A_2BB'O_6$ structure.

II. EXPERIMENTAL

Polycrystalline samples LaCo$_{1-x}$Rh$_x$O$_3$ with $x = 0$, 0.02, 0.04, 0.08, 0.2 and 0.5, were prepared according to the following procedure. Hot water solution of metal ions prepared by decomposition/dissolution of La$_2$O$_3$, RhCl$_3$.H$_2$O, and Co(NO$_3$)$_2$.6H$_2$O in 30% HNO$_3$ was mixed with in advance prepared citric acid (CA) - diethylene glycol (EG) water solution. The molar ratio CA:EG was 1:1 and the molar ratio (CA+EG):metal ions was also 1:1. Clear, transparent and voluminous aerogel was obtained after evaporation of water at 140°C. The gel was pulvurised in a mortar, dried, pyrolyzed, and organic carbon residue were removed by proper heat treatment at temperatures 180-450°C in a chamber furnace under static air atmosphere. After careful mixing and grinding, the final crystallization of LaCo$_{1-x}$Rh$_x$O$_3$ perovskite phase has been done by annealing at 1200°C for 100 hours in air atmosphere.

X-ray powder diffraction using a Bruker D8 diffractometer (CuK$_\alpha$ radiation, SOL-X energy dispersive detector, 2$\theta$ range 20° - 150°) was employed to determine the phase compositions and lattice and structural parameters. The diffraction patterns were analyzed with the Rietveld method using the FULLPROF program [11].

The magnetic properties were measured by means of a SQUID magnetometer MPMS-7 (Quantum Design) over the temperature range 4.2 – 300 K and a magnetosusceptometer DSM 10 (Manics) at elevated temperatures up to 800 K.

Thermal conductivity, thermoelectric power and electrical resistivity were measured using a four-probe method with a parallelepiped sample cut from the sintered pellet. The electrical current density varied depending on the sample resistivity between 10$^{-1}$ A/cm$^2$ (metallic state) and 10$^{-7}$ A/cm$^2$ (insulating state). The measurements were done on sample cooling and warming using a close-cycle cryostat working down to 3 K.

III. METHOD OF CALCULATION

The calculations were done with the WIEN2k program [12]. This program is based on the density functional theory (DFT) and uses the full-potential linearized augmented plane wave (FP LAPW) method with the dual basis set. The core states were defined as an electronic configuration (Kr, 4d$^{10}$) for La, (Ar, 3d$^{10}$) for Rh, (Ne, 3s$^2$) for Co and as (He) for O atoms. The valence states included 3p, 3d and 4s orbitals for Co, and 4s, 4p, 4d and 5s for Rh. All calculations were spin-polarized. For the exchange correlation potential the GGA form was adopted [13]. The radii of the atomic spheres were taken 2.3 a.u. for La, 2.05 a.u. for Rh, 1.95 a.u. for Co and 1.55 a.u. for O. To improve the description of Co 3d and Rh 4d electrons we used the GGA+U method, which corresponds to $LDA+U$ method described in [14] with the GGA correlation potential instead of $LDA$. The values of Coulomb and exchange parameters were used the same as in the previous studies, $U = 2.7$ eV and $J = 0$ eV, for both Co and Rh [2, 4]. The atom positions were optimized by minimization of the calculated forces on the nuclei [10].

The calculations were performed in order to test two specific cases - small doping of Rh in LaCoO$_3$ (and similarly small doping of Co in LaRhO$_3$) and $x = 0.5$. For the first case, an ordered arrangement of 1 Rh and 15 Co atoms was constructed ($x = 1/16$), simulating a rather isolated Rh atom in Co matrix. The model is characterized by intersected Rh-Co-Co-Rh... chains running along three pseudocubic axes, and a body centered supercell $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ is used in order to include the octahedral tilting ($a_p$ is a lattice parameter of the cubic perovskite cell). An analogous model structure for half doping $x = 1/2$ is of double perovskite type with 1:1 rock-salt arrangement of Co and Rh ions in the cubic supercell $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 2a_p$, characterized by intersected Rh-Co-Rh... chains. The inversion symmetry operation
was only retained in both cells.

IV. RESULTS

The symmetry of the unit cell is changed from rhombohedral \( R3c \) for small doping \( x = 0 - 0.08 \) to orthorhombic \( Pbnm \) for \( x = 0.2 - 1 \) in agreement with previous studies \[9, 10\]. The average bond distance \( Co,Rh-O \) increases and average bond angle \( Co,Rh-O-Co,Rh \) decreases as more rhodium is inserted in the structure, i.e. the octahedral tilting is enhanced with increasing doping, see Fig. 1a. These observations are in agreement with larger ionic radius of Co\(^{3+} \) (0.665 Å in six-fold coordination) compared to Co\(^{4+} \). Actually, the ionic radius of Co\(^{4+} \) significantly depends on its spin state (0.545 Å in LS and 0.610 Å in HS state), nevertheless Rh\(^{3+} \) is larger than Co\(^{3+} \) in any spin state.

The structural evolution of CoRh\(_6\) octahedra is manifested in the increase of cell volume with Rh doping, see Fig. 1b. The dependence shows a positive deviation from linearity in agreement with previous studies \[8, 9\]. This deviation could also be detected in the dependence of bond distances and angles, although it is mostly hidden within error bars because the accuracy of these values is much lower, since X-ray diffraction is very accurate in determination of lattice parameters, but is not as much sensitive to oxygen positions.

Electric resistivity has semiconducting character at low temperature for all \( x \), see Fig. 2a. A transition to a more conducting state is observed above 400 K for small Rh dopings, manifested by a peak in apparent activation energy around 500 K, see inset of Fig. 2. For \( x = 0.5 \), only a broad hump is observed in the activation energy. High thermoelectric power at low temperature indicates a low concentration of carriers, see Fig. 2b. The absolute value of Seebeck coefficient ranges from 400 to 800 \( \mu V/K \). A decrease to a metallic-like value \( \sim 30 \mu V/K \) is observed above 400 K for small Rh doping. In contrast, the Seebeck coefficient for \( x = 0.5 \) saturates at a higher value of \( \sim 100 \mu V/K \). Thermal conductivity is decreasing and the phononic peak at low temperature is suppressed with increasing Rh content, see Fig. 2c.

Magnetic susceptibility measured in DC field of 10 kOe is displayed in Fig. 3. The low-temperature transition to LS state is shifted down in temperature by approx. 35 K for \( x = 0.02 \) and it is suppressed for \( x = 0.04 \). It means that inserting Rh into LaCo\(_3\) destabilizes the purely LS ground state of Co. As can be deduced from the slope of inverse magnetic susceptibility at the lowest temperatures, a nonzero HS population is present starting from \( x = 0.04 \). The population of Co\(^{3+} \) in HS state is estimated between 14 – 18% with maximum for \( x = 0.2 \). The composition \( x = 0.2 \) deserves special attention, since the sample shows clear signatures of magnetic ordering.
The anomaly in transport data in the inset of Fig. 2a. completely vanishes, in agreement with the behavior of temperature with Rh doping, and for gradually diminished and shifted to slightly higher temperature, the samples observed within the range 150–300 K. At a higher temperature, the slope of inverse susceptibility is obtained as a result of the excitation of further HS states and interactions among them. Finally, practically linear behavior of inverse susceptibility is observed below 10 K, including the finite remanent magnetization in measurements of hysteresis loops, in agreement with the recent paper of Asai et al. [1].

With increasing temperature, the slope of inverse susceptibility is changed as a result of the excitation of further HS states and interactions among them. Finally, practically linear behavior of inverse susceptibility is observed within the range 150 – 300 K. At a higher temperature, the samples x = 0 – 0.2 exhibit a magnetic anomaly associated with the I-M transition. Its extent is gradually diminished and shifted to slightly higher temperature with Rh doping, and for x = 0.5 the transition completely vanishes, in agreement with the behavior of the anomaly in transport data in the inset of Fig. 2a.

In order to characterize the room-temperature phases of LaCo$_{1-x}$Rh$_x$O$_3$ in a more quantitative manner, let us discuss the results of the Curie-Weiss fit of inverse susceptibility within 150 – 300 K, which are summarized in Table I. It is seen that the effective magnetic moment $\mu_{eff}$ is enhanced for x = 0.02 compared to x = 0 and then it takes an opposite trend and is decreasing with x. The number of Co$^{3+}$ in HS state ($p_{HS}$, $S = 2$) can be calculated from the $\mu_{eff}$ presuming Rh$^{3+}$ and remaining Co$^{3+}$ ions in the non-magnetic LS state. The calculated $p_{HS}$ is reduced from 0.47 for x = 0.02 to 0.41 for 0.08 while the number of Co$^{3+}$ in LS state $p_{LS}$ is practically constant around 0.51, as though Rh were predominantly replacing Co$^{3+}$ in HS state for the small doping range of x. On the other hand, the extrapolation to x = 0 gives $p_{HS}$ = 0.49, which is a somewhat higher value than $p_{HS}$ = 0.46 actually determined for x = 0. The origin of this discontinuity can be rationalized as follows:

In the frame of the LS/HS thermal excitation model [1 3 17], the population of HS states in pure LaCoO$_3$ is limited to 50%, since probability of nearest HS neighbors is strongly suppressed. Because the excitations to HS state are dynamic and only a short-range correlated, the actual limit should depend on the size of the correlated clusters of alternating HS-LS states (or rather on the size of disordered boundaries between the clusters with Co ions in LS states), and should be somewhat lower than 50%. Therefore $\mu_{eff}$ corresponding to $p_{HS} \sim 0.46$ is observed. We suppose, that the clusters of alternating HS-LS states, which are stabilized by dilute Rh dopants representing immobile elastic defects, are larger than the thermally induced dynamic clusters, hence the sum of Rh$^{3+}$ and HS Co$^{3+}$ ($x + p_{HS}$) may approach closer the limit of 50%.

The decrease of $\mu_{eff}$ with higher doping of Rh (x > 0.08) is not so steep. In particular for x = 0.5, the calculated $p_{HS}$ only decreases to 0.35, while $p_{LS}$ is reduced down to 0.15. We suppose, that the reason is in cumulation of large Rh ions, which creates a positive lattice strain and thus supports HS state on nearby Co sites. This effect of Rh dopants for stabilization of HS state at neighboring Co ions prevails for higher x → 1, whereas the previously mentioned effect of Rh ions replacing HS Co ions in LS/HS ordered regions and supporting HS state on the next neighbor Co sites dominates for lower x → 0. Nevertheless, in both cases the HS states stabilized by Rh, unlike those obtained by thermal excitation, are preserved down to the lowest temperature.

The dependence of cell volume on x would be linear if the room temperature ratio $p_{HS}$ : $p_{LS}$ remained constant at the original x = 0 value for all x. Since this ratio becomes higher in the doping region x = 0.2 – 0.5 (and presumably also for x > 0.5), the observed cell volume show a marked positive deviations, see Fig. 1b.

The Weiss $\theta$ deduced from the susceptibility data over the range 150 – 300 K are negative for all x and the absolute values are approximately decreasing with $p_{HS}$, as expected regarding the antiferromagnetic interaction between Co$^{3+}$ in HS state.

The table shows calculated populations of HS and LS states.

| x(Rh) | $\mu_{eff}$ (µB) | $\theta$(K) | $p_{HS}$ | $p_{LS}$ |
|-------|------------------|-------------|----------|----------|
| 0     | 3.31             | -203        | 0.46     | 0.54     |
| 0.02  | 3.35             | -189        | 0.47     | 0.51     |
| 0.04  | 3.25             | -140        | 0.44     | 0.52     |
| 0.08  | 3.14             | -146        | 0.41     | 0.51     |
| 0.2   | 3.10             | -159        | 0.40     | 0.40     |
| 0.5   | 2.89             | -148        | 0.35     | 0.15     |
The previous GGA+U calculations evidenced, that two magnetic phases may exist in LaCoO$_3$ perovskite, in addition to the non-magnetic LS ground state. The first one is a result of gradual population of HS states conditioned by presence of the LS states at the nearest Co sites. Nevertheless, some Co(HS) pairs do exist and are responsible for prevailing antiferromagnetic interactions. The HS state in LS matrix is further stabilized if Co(HS) site is expanded (breathing-type) at the expense of neighboring Co(LS) sites. The mixed LS/HS phase tends to a short-range ordered 1:1 arrangement, whose long-range formation is presumably prevented by the entropy factor. The second phase consists of large IS clusters, which may exist within the LS/HS phase and finally tend to a formation of uniform itinerant IS phase with ferromagnetic coupling. The cell volume expansion destabilize the LS ground state and for certain critical volumes the energy of LS/HS phase or IS phase become lower.

In the present GGA+U calculation, several spin states configurations of Co were tested using the La$_{16}$Co$_3$RhO$_{18}$ supercell ($x = 0.0625$), namely:

1. All Co ions in LS state.
2. All Co ions in IS state.
3. Co in LS and HS state in 1:1 ratio, with the 6 nearest Co around Rh in LS state, see Fig. 4a, displaying the nearest neighbors (Co LS) and the next nearest neighbors (Co HS).
4. Co in LS and HS state in 1:1 ratio, with the 6 nearest Co around Rh in HS state, see Fig. 4b.

Spin moment of Rh was allowed to vary, nevertheless it always converged to LS value. Cell volumes were adopted to values expected for various doping by interpolation between LaCoO$_3$ and LaRhO$_3$. Atom positions determined at room temperature were used as the initial values and all refinable coordinates were optimized. The cell volume was also decreased by 1-2% to simulate the cell contraction with temperature ($T \to 0$ K).

Fig. 5 shows a comparison of the calculated energies for the LS/HS configuration and homogenous IS phase relative to the LS phase, depending on the perovskite cell volumes of LaCoO$_3$ and LaCo$_{15/16}$Rh$_{1/16}$O$_3$.

The cell volume of LaCoO$_3$ at 5 K is about 2% smaller compared to room temperature [13], however only 1% is related to temperature induced contraction and another 1% is related with the reduction of the Co$^{3+}$ size at the spin transition [20]. Since the spin transition in LaCo$_{1-x}$Rh$_x$O$_3$ is incomplete, the maximum volume contraction is expected between 1 – 2% in this case. The relative cell volumes approximately corresponding to $T = 0$ K are indicated in the figure. In both cases, the lowest energy state at room temperature (volume $V_{RT}$) is LS/HS, but the stabilization energy, relative to LS state, is higher for Rh-doped compound. With the volume contraction simulating the temperature decrease, the LaCoO$_3$ system undergoes a crossover at about 99.4% volume to the LS ground state, while this crossover for LaCo$_{15/16}$Rh$_{1/16}$O$_3$ is around 98.7% volume, which is almost $T \to 0$ K in this case.

These calculations thus evidence that the LS/HS state is stabilized upon rhodium doping. The driving force of this stabilization is the elastic energy. The ionic radius of Co$^{3+}$ strongly depends on the spin state. This is confirmed by GGA+U structure optimization, which gives Co-O bond lengths 1.92 Å and 1.97 Å for LS and HS states, respectively. The optimized Rh-O bond length is around 2.02 Å. Inserting Rh to Co matrix therefore brings about an increase of elastic energy, which is relaxed by keeping the nearest Co neighbors in LS state and exciting the second nearest Co neighbors do HS state, creating locally ordered cluster of large cations (Rh$^{3+}$ and HS Co$^{3+}$) and small cations (LS Co$^{3+}$), see Fig. 4c. The alternative LS+HS state configuration, see Fig. 4d, is evidently less favorable regarding the elastic energy, as it was confirmed by the calculations.

Calculation for the $x = 0.5$ within the La$_4$Co$_2$Rh$_2$O$_{12}$ supercell suggests that the LS Co$^{3+}$ state is stable for $T \to 0$, energies of HS and LS state become comparable at around the room temperature, and HS state is stabilized at elevated temperatures, i.e. upon further increase of the unit cell volume.

The calculation simulating the rhodium-rich limit $x \to 1$, i.e. using the La$_{16}$Co$_3$RhO$_{18}$ supercell (see Fig. 4c), shows that in this case the HS state of Co is more stable.
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than LS state. This result can be understood considering that isolated LS Co$^{3+}$ in the lattice of much larger Rh$^{3+}$ ions would represent an elastic defect of large energy cost.

The results of GGA+U calculations are in agreement with magnetic susceptibility analysis. For small doping the Rh atoms stabilize the HS states of cobalt at the next-nearest sites due to the elastic energy, therefore the low-temperature transition to pure LS state is suppressed. But at the same time, Rh ions actually occupy places which would be otherwise available for HS Co$^{3+}$, thus the saturated number of Co in HS state is lowered with the doping and number of Co in LS state is retained.

According to LS-LS/HS-IS model, the high temperature spin transition is based on formation of uniform IS phase. Thus the destabilization of the IS state by Rh doping (Fig. 6) is in agreement with suppression of this transition evidenced by magnetic data.

In order to investigate the relative role of elastic energy associated with larger Rh$^{3+}$ size and purely electronic effects, additional simulations have been performed for $x = 1/16$ doping of other isovalent dopants with different ionic radii - Al$^{3+}$ ($r_{Al} = 0.535$), Ga$^{3+}$ ($r_{Ga} = 0.62$) and In$^{3+}$ ($r_{In} = 0.80$). Cell volumes were adopted to expected values for $x = 1/16$ doping by interpolation between LaCoO$_3$ and respective LaMO$_3$. Atom positions determined at room temperature were used as the initial values and all refinable coordinates were optimized. The cell volume was also decreased by 1-2% to simulate the cell contraction with temperature. The results are presented in Fig. 6. It is seen that the stabilization energy of the LS/HS configuration with respect to pure LS phase is proportional to the ionic radius of the doping cation in the Al, Ga and In doped systems, but in the case of Rh there is an additional energy gain, obviously due to electrons of unfilled shell 4d and their covalency.

Total and atom projected density of states (DOS) of LaCo$_{1-x}$Rh$_x$O$_3$ ($x = 1/16$) for LS spin configuration is displayed in Fig. 7. The character of DOS is insulating.

Total and atom projected density of states (DOS) of LaCo$_{1-x}$Rh$_x$O$_3$ ($x = 1/16$) for LS spin configuration is displayed in Fig. 8. The character of DOS is insulating.
with a gap about 0.8 eV. The narrow states 0−0.25 eV below $E_F$ correspond to Rh($t_{2g}$), whereas Co($t_{2g}$) and O($p$) states are situated lower in energy between 0.25−1 eV. The states just above Fermi level are mainly of Co character. DOS of LS/HS spin configuration is displayed in Fig. 5. The insulating character of DOS is retained with a slightly decreased gap about 0.5 eV. The narrow states corresponding to Rh($t_{2g}$) are also within the energy range 0 − 0.25 eV below $E_F$, and the states of Co-LS($t_{2g}$) and O($p$) could be found lower in energy between 0.25−1 eV. A sharp peak above Fermi level belongs to Co-HS($t_{2g}$) band.

It was assumed in the previous discussion, that there is no charge transfer between Co$^{3+}$ and Rh$^{3+}$. To estimate quantitatively charge equilibria in our GGA+U calculations we use Atoms In Molecule (AIM) concept of Bader [21]. In this approach the unit cell is divided into regions by surfaces that run through the minima in the charge density. The charge on a given site is obtained by integrating the electronic density within these regions. The advantage of this method is that the analysis is based solely on the charge density, so it is independent on the basis set and atomic spheres used.

The ionic charges calculated by the AIM method differ from the formal valencies due to hybridization between cations and oxygen. The ratio of the AIM and ideal charge may be regarded as the degree of hybridization. Therefore, a different AIM charge of cations with nominally equal valencies can be solely caused by a different degree of hybridization with oxygen, and cannot be directly considered as a charge transfer between the cations. Instead, we compare calculated AIM charge of Co in undoped and doped structures. The AIM charges of cobalt in LaCoO$_3$ are within 1.40 − 1.64 depending on the its actual spin state, since the hybridization with oxygen is predominantly based on $e_g$ orbitals and thus depends strongly on their occupation, which is different for each spin state. Essentially the same AIM charges of Co are obtained for doped structure LaCo$_{1-x}$M$_x$O$_3$ ($x=1/16$), in spite of the various values calculated for the substituting cations M, namely Rh (1.33), Al (1.98), Ga (1.94) and In (1.88). It means that the difference between AIM charge of nominally Co$^{3+}$ and Rh$^{3+}$ in LaCo$_{1-x}$Rh$_x$O$_3$ solely account for the different degree of hybridization of Rh and Co, but not present any ground for the charge transfer between Co and Rh.

V. CONCLUSION

The present experiments supported by GGA+U electronic structure calculations provide strong arguments that the transition metal ions in the LaCo$_{1-x}$Rh$_x$O$_3$ solid solutions remain in trivalent states. The GGA+U calculations suggest that the elastic coupling of the nearest and next-nearest cobalt neighbors of the inserted Rh dopant is important in stabilization of the spin-state configurations. The Rh$^{3+}$ ions are always in the non-magnetic LS configuration, while the Co$^{3+}$ ions may vary, depending on composition and temperature, between the non-magnetic LS and paramagnetic HS local configurations. In distinction to pure LaCoO$_3$, in which HS Co$^{3+}$ states only appear at increased temperature through a thermal activation process, the Rh doped systems starting from $x=0.04$ exhibit certain number of stable HS Co$^{3+}$ species already in the ground state (up to 18% for $x=0.2$). The HS population increases gradually with increasing temperature and reaches a saturation above 150 K, similarly to what is observed in undoped LaCoO$_3$. The resulting phases, based on the LS/HS disproportionated cobalt sites, persist at least up to room temperature. A gradual transformation to a uniform state with metallic-like conductivity is evidenced at elevated temperatures for samples with $x<0.5$.

The main characteristics of the room-temperature phase of LaCoO$_3$ is the LS/HS population close to the 1:1 ratio. This can be understood as a result of cooperative effects, which prefer a regular ordering of smaller LS Co$^{3+}$ ions and larger HS Co$^{3+}$. Nevertheless, only short-range LS/HS correlations are anticipated considering the entropy reasons. Similar ordering tendencies also exist in the doped systems but the mechanism is different. The primary HS population arises from the elastic strain associated with presence of immobile Rh dopants. The strain is released by stabilization of LS states on the nearest cobalt neighbors and HS states on the next nearest ones. These clusters grow as additional HS states are thermally activated and tend to a saturation in which small LS Co$^{3+}$ ions alternate with HS Co$^{3+}$ and LS Rh$^{3+}$ ions of larger size. The stability of such arrangement can be related to two factors. The first one is the known property of double perovskite structure $A_2BB'O_6$ to adapt to very different radii of $B$ and $B'$ cations. This is a kind of elastic energy optimization, which is effective not only for the rhodium but also for other large isovalent dopants like In. The second mechanism is of purely electronic origin and is associated with incomplete character of the 3$d$ and 4$d$ shells of Co and Rh ions.

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