Valence states and associated features of Co in quasi-one-dimensional Ca₃Co₂O₆

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The valence state of the constituents of Ca₃Co₂O₆ has been analyzed using accumulated charge in atomic spheres and Bader regions as well as Born effective charges, and the results are compared with the situation in CoO and LaCoO₃ where Co takes a divalent and trivalent state, respectively. Moreover, the role of the covalent contribution to the bonding between Co and O and the possible metallic bonding between the Co atoms on the magnetic ordering and valence states has been investigated with the help of orbital-projected DOS, charge density, charge transfer, and electron-localization function. Born-effective-charge analyses show that the actual valence of the Co atoms are much smaller than the often believed 3+ state and the valence characteristics are highly directional dependent, in fact about three times more pronounced along the chains than perpendicular to the chains.

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I. INTRODUCTION

Low-dimensional structures have long been acknowledged to exhibit intriguing transport and magnetic properties. Recently, attention has been focused on quasi-one-dimensional phases [1] with the general formula $A_1T_1T_2O_6$ ($A = \text{Ca, Sr, Ba};T_1T_2 = \text{transition metal}$) where transition-metal-oxygen polyhedra form well separated chains running parallel to the trigonal axis of the crystal structure. In Ca₃Co₂O₆, which is the target of this study, each chain consists of alternating, face-sharing Co₆ octahedra (Co₁O₆$^{\alpha}$) and CoO₆ trigonal prisms (Co₂O₆$^{\beta}$). Typically, the ratio of the interchain to intrachain metal-metal distance is of the order of two giving the structure its quasi-one-dimensional character. The Ca atoms are located in the regions between the chains. Within this class of oxides, Ca₃Co₂O₆ is the only representative in which T1 and T2 refer one and the same element. Magnetic properties of Ca₃Co₂O₆ have been clarified to some extent, whereas aspects like valence states are still open for considerable debate. The fact that there are two different Co sites in the crystal structure makes it difficult to fully penetrate the nature of the electronic state of the individual Co atoms.

The possible valence states for Co are one, two, three, and four associated with various spin states such as low-spin (LS), intermediate-spin (IS) or high-spin (HS), and different spin, charge, and orbital ordering with different structural dimensionality. These are responsible for various interesting phenomena such as the temperature-induced spin-state transition in LaCoO₃ [2], the colossal magnetoresistance in La$_{1-x}$Sr$_x$CoO₃ [3], the insulator-metal transition and magnetoresistance properties in the oxygen-deficient perovskite phase LaBaCo₂O$_{5.5}$ [4], and the high figure of merit for the conversion of thermoelectric energy in the two-dimensional material Ca₃Co₄O₉ [5].

The crystal structure of Ca₃Co₂O₆ is related to the K₄CdCl₆-type structure [6] (space group R3c) and consists of (Co₂O₆)$^\infty$ chains of alternating face sharing CoO₆ octahedra and Co₂O₆ trigonal prisms along the hexagonal c axis. Each (Co₂O₆)$^\infty$ chain is surrounded by six corresponding chains forming a triangular net in the ab plane. The adjacent Co$^2+$ atoms experience strong ferromagnetic (F) coupling within the chains whereas the interchain coupling is weakly antiferromagnetic (AF) [7–11]. Thus, relevant magnetic properties of Ca₃Co₂O₆ can be described in terms of a planar Ising hexagonal lattice in which the magnetic moment of each (Co₂O₆)$^\infty$ chain can be rationalized with one accumulated spin.

We have earlier reported electronic structure calculations for Ca₃Co₂O₆ in the ground-state ferrimagnetic (Ferri) structure [12], and the calculated total moment was found to be in very good agreement with low-temperature powder neutron diffraction [7] and the magnetization measurements [13]. Even though several theoretical studies [14–19] have been performed on Ca₃Co₂O₆, nobody (except our previous work [12]) has attempted to base the study on the experimental ground-state Ferri structure of this compound. This neglect is of course explicable on the ground of the complex magnetic structure which makes the electronic structure computations quite demanding. So, our previous report [12] represents the only theoretical account for Ca₃Co₂O₆ in the correct ground state.

It is generally agreed that Ca will be in the 2+ state and O in the 2− state in this class of compounds. Hence, in order to make charge balance, Co₁ and Co2 take here either a pure ionic 3+ state (alternatively 2+ and 4+ states) or less than 3+ if the bonding with the O neighbors takes a significant degree of covalent character. On the basis of the T1-O/T2-O bond lengths in Ca₃Co₂O₆ [6] and corresponding phases [20, 21] it was predicted that the Co$^2+$ has a much lower oxidation state than Co$^3+$ because the Co-O bonds in the trigonal prisms

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are longer than those in the octahedra. An implicit assumption made during these deductions is that the T2-O bond length is not affected by the magnetic state and/or covalent bonding interaction. The higher-lying d levels for the T2O6 configuration has a stronger antibonding character and more of these levels are occupied in a high-moment (HM; note that we by purpose avoid the conventional notation HS) state than in a low-moment (LM) state. As a result the TO6 configuration should have longer T-O bond lengths in a HM state than a LM state.

In our previous study [12] we concluded that CoI and CoII in Ca3Co2O6 are in valence state four and two, respectively. We will now elaborate on reasons behind this inference. It is established that one can substitute Co with four-valent species such as T = Mn, Ru, Rh, or Ir up to (or near) the composition Ca3CoT06 [22–25]. It is also shown that it is possible to simultaneously substitute both two- and four-valent species in this structural framework [26–28]. These observations suggest that it is chemically plausible to have Co ions with valence states two and four in Ca3Co2O6.

In an octahedral (cubic) crystal field the Co-d levels will split into triply degenerate t2g (dxy, dxz, dyz) and doubly degenerate eg (dx2−y2, d2z2−r2) levels. Owing to trigonal distortion of the octahedral co-ordination, the t2g levels further split into a non-degenerate 1a level and doubly degenerate 1e levels. With Co in the 4+ oxidation state there will be five d electrons to accommodate in these levels. The spin moment according to a pure ionic description will then be 1, 3, and 5 μB per Co for low-spin (LS; t2−g eg), intermediate-spin (IS; t2−g eg), and high spin (HS; t2−g eg) configuration, respectively. In practice, materials often have covalent hybridization between the transition metal and surrounding atoms, and this will reduce the spin moment owing to the fact that some of the electrons participate in bonding rather than in magnetism. So, one mostly gets non-integer value for the spin moments at the transition metal sites and also small induced moments at the sites of the surrounding atoms.

A powder neutron diffraction study [7] of Ca3Co2O6 shows that, in the ordered magnetic state, the magnetic moment at the CoI site is 0.08 ± 0.04 μB. The calculated spin moment for the CoI site obtained from accurate density-functional calculation is 0.169 μB [12] (note that calculated magnetic moments generally are smaller than those obtained by magnetization measurements). With Co in a 3+ LS state (t2−g eg) one expects zero spin moment at the CoI site. However, the t2g states should have been completely filled and the eg states completely empty; features not seen in any of the reported orbital-projected density-of-states (DOS) data [14, 19]. We laid decisive weight on the DOS evidences and concluded [12] that CoI is in a 4+ LS state. The too small value for the spin moment compared with the ionic picture was attributed to the strong covalent contribution to the bonding between CoI and O.

In a trigonal prismatic crystal field d levels will split into non-degenerate 1a (d2z), doubly degenerate 1e (dxz, dx2−y2), and doubly degenerate 2e (dxy, d2z−r2) levels. With Co in the 2+ oxidation state there will be seven d electrons to be accommodated in these levels. The spin moment for CoII in LS (1a−t e−t 2e−t) and HS (1a−t e−t 2e−t) configurations will then be 1 and 3 μB, respectively, for the pure ionic case. The powder neutron diffraction study [7] gave an ordered magnetic moment at the CoII site of 3.00 ± 0.05μB, whereas the density-functional calculation gave a somewhat smaller spin moment (2.632μB). The calculated total moment for Ca3Co2O6 in the Ferri state came out in very good agreement with the experimental value (1.209 vs 1.30μB). As the calculated spin moment for both Co atoms came out in reasonably good agreement with ionic Co⁺⁺, LS and Co⁺⁺, HS states we jumped to the conclusion of 4+ and 2+ oxidation states for CoI and CoII in LS and HS configurations, respectively. Recently there have appeared several experimental [8, 25, 30, 31] and theoretical [14–16, 19, 32, 33] reports claiming that the valence states of both Co atoms in Ca3Co2O6 are in fact 3+. So, in order to get more insight into the valence states of Co we have now made more detailed theoretical analyses of the Co valence situation in Ca3Co2O6.

II. COMPUTATIONAL DETAILS

The crystal-orbital-Hamiltonian-population (COHP) and electron-localization-function (ELF) data were calculated using the TBLMTO program [34]. For the DOS calculations we have applied the full-potential linearized-augmented plane-wave method implemented in the WIEN2k package [35] including spin-orbit coupling. The Born-effective-charge calculations were performed using the Vienna ab-initio simulation package (VASP) [36] within the projector-augmented-wave (PAW) method [37] as implemented by Kresse and Joubert [38]. Structural optimizations were continued until the forces on the atoms had converged to less than 1 meV Å−1 and the pressure on the cell had minimized within the constraint of constant volume. The optimized structure has been used for the Berry-phase calculations. The atoms involved in the calculations required extra care: either large basis sets within a pseudo-potential scheme or an all-electron scheme. So we have used very large basis sets with 875 eV for the plane-wave cutoff. For the k-space integrations in the Berry-phase calculations, a uniform 8 × 8 × 8 k-point mesh was found to be adequate. For LaCoO3 and CoO, we have used the LDA+U approach with an U value of 5 and 8 eV, respectively, for Co in order to reproduce the insulating behavior.

III. RESULTS AND DISCUSSION

Before we pursue our renewed findings we will give a brief account of the recent development in the view on the spin and valence situation in Ca3Co2O6. Essentially
only one new aspect on the magnetism of Ca$_3$Co$_2$O$_6$ has come into the picture since we published our previous report [12]. A recent study [39] by the muon spin rotation and relaxation technique shows that there occurs a magnetic transition already at \( \sim 200 \text{K} \). This feature (which is not detected by powder neutron diffraction [7]) has been attributed to short-range one-dimensional F ordering within the (Co$_2$O$_6$)$_{\infty}$ chains. Below \( \sim 100 \text{K} \) this ordering scheme is then assumed to develop further into a short-range two-dimensional AF pattern, which in turn converts into a co-operative AF state. At least two magnetic transitions are recognized at quite low temperatures. One around 24 K can rather unambiguously be attributed to F ordering within the chains and another around 10 K appears to be associated with Ferri coupling between the chains [7, 8]. The origin of the latter transition remains a matter of dispute [7, 8, 22, 28, 40, 41], some reports favoring a more regular Ferri situation with interchain AF coupling between the F chains [7, 40] while others point at spin-glass freezing within every third chain [42]. On the basis of a moment of 4 \( \mu_B \) per Ca$_3$Co$_2$O$_6$ formula unit from magnetization measurements [43], it has been conjectured that both Co atoms are in a 3+ state with Co$^{1+}$ as LS (non-magnetic) and Co$^{2+}$ as HS (magnetic). The effective moment has been extracted from the temperature dependence of the magnetic susceptibility and explained as a 1:1 HS and IS configurations of Co in 3+ states [8]. This interpretation is in the first place contradictory to the neutron diffraction results [7] and secondly stabilization of the IS configuration requires lowering of the symmetry of the Co$^{1+}$ co-ordination in order to provide the required additional splitting of the \( e_g \) levels. Also, Co in a pure 3+ IS state should have a moment of 2 \( \mu_B \) and introduction of covalence should reduce the moment, but probably not below 1 \( \mu_B \) (see Ref. [2]). All in all, the fresh magnetic data suffer from exactly the same weaknesses as the older data with regard to evaluation of the valence states for Co$^{1+}$ and Co$^{2+}$ (see below).

X-ray photoemission spectroscopy (XPS) data on Ca$_3$Co$^x$TO$_6$ \((T = \text{Co, Rh, Ir})\) have been interpreted [25] as evidence for a 3+ valence state for Co$^{1+}$ and Co$^{2+}$ in LS and HS configurations, respectively. XPS profiles comprise information about the DOS of the electrons, but it is very difficult to judge oxidation states from such data alone. Even extraction of qualitative valence-state information from XPS data requires the use of suitable standards for comparison. Such references have apparently not been used in this case. As mentioned before, the crucial information needed to decide the valence state is the orbital-projected DOS and that can not be extracted from the XPS. Moreover, the XPS measurements were carried out at room temperature and at this temperature it is quite possible that Co has in any case reached a common average valence state. Hence, the conclusion advanced from XPS measurements can not be taken as conclusive evidence for a 3+ universal oxidation state for both Co atoms in Ca$_3$Co$_2$O$_6$.

Low-temperature field-sweep $^{59}$Co NMR measurements on Ca$_3$Co$_2$O$_6$ have also been interpreted [30] as evidence for the presence of non-magnetic Co in the 3+,LS state. A serious drawback with this study is that only the signal from one of the two Co sites is detected and even this signal could only be observed in a very narrow temperature range from 7 to 15 K. The key questions in this connection are then why the signal from the companion 3+,HS state is not detected and what happens to the signal from the claimed 3+,LS state below 7 and above 15 K. Before these questions are satisfactorily answered the NMR findings can not be taken in favor of anything. However, one further comment of direct relevance for the present communication should be made. It is not possible to have completely non-magnetic Co species in Ca$_3$Co$_2$O$_6$ for the following reason. The shortest Co-Co distance within the chains is about 2.59 Å which is comparable to that in the closest Co-Co distance in hcp Co \((2.51 \text{Å})\). Both experimental [7] and theoretical [12] studies clearly demonstrate that Co$^2+$ carries a large spin moment. Hence, one can not conceive a situation with a completely non-magnetic Co$^{1+}$; the large moment at Co$^2+$ site and the short Col-Co$_2$ distance, should certainly have led to an induced moment at the Co$^{1+}$ site.

Recently two reports [18, 19] have appeared dealing with LDA+$U$ calculations on Ca$_3$Co$_2$O$_6$. It is therefore appropriate to consider any drawbacks using the LDA+$U$ method on Ca$_3$Co$_2$O$_6$. The degree of localization of the electrons at the Co$^{1+}$ and Co$^{2+}$ sites are not the same and hence the use of the same \( U \) and \( J \) values for both sites is not appropriate. Furthermore, the quasi-one-dimensional nature of the atomic arrangement also gives the band dispersion a one-dimensional character. So, in order to treat the strong correlation effect in Ca$_3$Co$_2$O$_6$ appropriately one needs to account for the \( k \) dependence of \( U \). viz. the Mott-Hubbard correction terms in the LDA+$U$ methods must contain local character, features missing in the currently available LDA+$U$ approach. With these deficiencies, the LDA+$U$ calculations will inevitably reveal that the relative stability of the intrachain F and AF arrangements depends on the chosen \( U \) value and the “initial density” employed for the calculations [18]. For example, the intrachain F arrangement is more stable than the intrachain AF arrangement for \( U = 3 \) and 4 eV, but the opposite is true for \( U = 2 \) and 5 eV. Moreover, the LDA+$U$ calculation gave a too large spin moment for the F state of Ca$_3$Co$_2$O$_6$ [19] \((5.66 \mu_B \text{f.u.}^{-1})\) compared with the magnetization measurements \((4 \mu_B \text{f.u.}^{-1})\) [43]. The use of LDA+$U$ calculations for Na$_3$CoO$_2$ [44] shows that caution must be taken in order to avoid worse agreement with experimental data than by the use of simple LDA calculations. In addition, it should be recalled that \( U \) is an empirical parameter. We have shown earlier [12], that the magnetic properties of Ca$_3$Co$_2$O$_6$ can correctly be described by the use of GGA itself. Therefore, in the following we will focus only on results obtained by GGA calculations.
Both the neutron-diffraction study [7] and our earlier total-energy calculations [12] show that Ca$_3$Co$_2$O$_6$ has a ferri ground state at 0 K. Specific heat [28] and transport measurements [45] show metallic behavior for Ca$_3$Co$_2$O$_6$. In contrast, the recent theoretical study [19] incorrectly concluded that this material is an F insulator. In our previous report we emphasized that all results reported had been obtained from relativistic full-potential GGA calculations with spin-orbit coupling (SOC) included. However, Ref. [19] wrongly cited that SOC had not been included in our calculations. All in all, we strongly believe that the GGA approach with spin-orbit coupling is sufficiently accurate to describe the electronic structure and magnetic properties of Ca$_3$Co$_2$O$_6$ and proceed our analysis accordingly.

To obtain firm pictures of the valence states of atoms in compounds, the key information one really needs is how many electrons that are present at each site in the atomic arrangement. This information is very difficult to extract unambiguously from usual DFT calculations owing to the fact that the integrated charges at a given site depends not only on the chosen radius for the enclosing atomic sphere, but also involve charges in the surrounding interstitial regions. In order to remedy this situation we have now consulted several tools, viz. charge density, charge transfer, electron-localization function, angular-momentum and orbital-projected DOS, crystal-orbital-Hamiltonian population, Bader charge, and Born effective charge. These analyses were carried out not only for Ca$_3$Co$_2$O$_6$, but also for CoO and LaCoO$_3$ (for which the valence states of Co are more unambiguous) in order to cross check their resolving capabilities.

More insight into the spin and valence states of the Co$^{1+}$ and Co$^{2+}$ atoms in Ca$_3$Co$_2$O$_6$ is provided by the orbital-projected d-electron DOS (Fig.1). This illustration clearly convey the message that Co$^{1+}$ is in a LM state, and Co$^{2+}$ conversely in a HM state. If Co$^{1+}$ had
been in a proper ionic 3+.,LS state one should expect that three $d$ orbitals would have been completely filled and two $d$ orbitals completely empty. On the contrary Figs. 1 and 2 show almost equal amounts of DOS in all $d$ orbitals, thus confirming that Co1 is certainly not in an ionic 3+,LS state. However, the partial DOS for Co1$^+$ and Co2$^+$ (Fig. 2) are sufficiently different to defend the characterization as different valence states. The partial DOS for Ca (Fig. 2) clearly demonstrates a nearly empty valence band and consequently an ideal 2+ state with negligible amounts of valence electrons at the Ca site. The energetically degenerate nature of the Co-$d$ and O-$p$ states conveys evidence for appreciable covalent interaction between Co and O, and as a result of this hybridization interaction there occur an induced spin moment of around 0.13 $\mu_B$ at the oxygen sites.

LaCoO$_3$ provides an example of Co$^{3+}$ in an LS state with completely filled $t_{2g}$ states and empty $e_g$ states and a resulting semiconducting behavior with a band gap of about 0.2 eV. As part of the control tests for Ca$_3$Co$_2$O$_6$ we have now calculated the DOS for the 3+,LS state for Co in LaCoO$_3$ and compared it with the DOS for the Co$^{1+}$ site. A similar comparison have been made for the DOS for the 3+,HS state of Co in LaCoO$_3$ (obtained from the fixed-spin calculation reported earlier [2]) in relation to that for Co$^{2+}$ in Ca$_3$Co$_2$O$_6$. These comparisons can be appraised in Fig. 3, which shows that there is certainly no correspondence between the Co DOSs obtained for the different modifications of LaCoO$_3$ and those for different sites in Ca$_3$Co$_2$O$_6$. The Co partial DOSs for Ca$_3$Co$_2$O$_6$ occur in narrower energy regions than those for the LaCoO$_3$ reference materials, overall features which we attribute to the quasi-one-dimensional nature of the crystal structure of Ca$_3$Co$_2$O$_6$.

If a given material exhibits a significant amount of covalence in its bonding, the simple oxidation state approach can not be used to estimate the valence states. All earlier studies on Ca$_3$Co$_2$O$_6$ have ignored the covalent contribution to the bonding and most of them have in fact made the valence assessment only on the observed size of the magnetic moments at the Co sites. Whangbo et al. [14, 18] made spin-polarized electronic band-structure calculation for Ca$_3$Co$_2$O$_6$ on the basis of the room-temperature crystal structure in F configuration. From partial DOS analyses these authors concluded that both Co$^{1+}$ and Co$^{2+}$ are 3+ ions in LS and HS state, respectively. However, this inference contradicts their own findings: (i) Despite the fact that the calculations gave a magnetic moment of 0.3 $\mu_B$ at the Co$^{1+}$ site they proceed as if the moment is zero. (It is worthwhile to record that DFT-calculated moments generally come out smaller than according to the pure ionic scheme due to the covalent interaction between constituents.) (ii) In an octahedral crystal field, proper Co$^{3+}$ ions in the LS state should exhibit completely filled $t_{2g}$ levels and completely empty $e_g$ levels. However, the orbital-projected DOS of Whangbo et al. closely resembles our findings (Figs. 1 and 2) which is clearly incompatible with a 3+,LS state.

Strength of bonding interaction between the constituents of a compound is often assessed from COHP plots. The COHP is the DOS weighted by the corresponding Hamiltonian matrix elements and is also indicative of the character of a bond (negative COHP indicating bonding; positive COHP antibonding interaction [34, 46]). The calculated COHP for the Co1-to-O, Co2-to-O, and Co1-to-Co2 interactions in Ca$_3$Co$_2$O$_6$ are illustrated in Fig. 4 which shows that the strongest

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig3}
\caption{(Color online) Calculated partial ($d$) density of states (DOS) for Co$^{1+}$ and Co$^{2+}$ in Ca$_3$Co$_2$O$_6$ for the ferrimagnetic ground-state phase superimposed with the calculated profiles for Co$^{3+}$ in LS and HS modifications of LaCoO$_3$, respectively. The Fermi level is set to zero.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{fig4}
\caption{(Color online) Crystal-orbital-Hamilton population (COHP) for Co1-to-O, Co2-to-O, and Co1-to-Co2 interactions in an assumed non-magnetic state of Ca$_3$Co$_2$O$_6$.}
\end{figure}
bonding interaction is between Co1 and O. This is consistent with the experimental findings in the sense that the Co1-O bond length is shorter than the Co2-O bond length. The integrated COHP yielded bond strength of $-1.39$, $-0.77$ and $-0.08$ eV for the Co1-to-O, Co2-to-O, and Co1-to-Co2 interaction, respectively. Since the covalent Co1-to-Co2 interaction is weak, the intrachain F interaction has to be attributed to metallic type of bonding. The strong covalent interaction between Co1 and O could explain why the spin moment at the Co1° site is quenched.

More details about the bonding interactions between constituents can be obtained from charge-density, charge transfer, and ELF analyses. The charge-density distribution in Ca$_3$Co$_2$O$_6$ [Fig. 5(a)] shows that only a negligibly small charge is left at the Ca site, thus confirming the presence of ionic bonding between Ca and the (Co$_2$O$_6$)$_\infty$ chains. The atoms within the chain exhibit appreciable covalent character as already manifested by the one-dimensional appearance. Although the interatomic Co1-Co2 distance is short, the interaction between these atoms are largely of metallic character. The charge-transfer distribution [Fig. 5(b)] shows that electrons are transferred from both Ca and Co atoms to the oxygen sites, viz. in accordance with an ionic conception. However, if the bonding interaction between Co and O had been purely ionic one would have expected an isotropic charge-transfer distribution. Hence, the anisotropic distribution between Co and O in the charge-transfer plot supports the inference that there is an appreciable degree of covalence in the Co-to-O bonding interaction. If one had known the amount of electrons transfer from Co to O, one could have estimated a more exact valence state for Co. According to Fig. 5(b) it is clear that both Co atoms have donated electrons to the oxygen sites, but the degree of charge transfer is different for Co1° and Co2°. In conclusion, it is difficult to judge the valence of Co from the charge-transfer distribution alone.

ELF is an informative tool to distinguish different bonding interactions in solids [47]. The ELF for Ca$_3$Co$_2$O$_6$ [Fig. 5(c)] exhibits only a small numerical value between Ca and the other constituents which is another indication for the ionic character of the Ca-to-(Co$_2$O$_6$)$_\infty$ bonding. The maximum value of the ELF at the O sites and minimum values at the Ca and Co sites reconfirms that charge has been transferred from Ca and Co to O. The polarization with different orientation of ELF at the Co sites indicates different orientation of the orbitals residing at Co1° and Co2°. Although the charge-density plot exposes a relatively large amount of charge at the Co sites, the small value of ELF show that these charges are mainly of $d$ character. The conclusion from the charge-density, charge-transfer, and ELF analyses is accordingly that the bonding interaction between Ca and O is mainly ionic and that between Co and O is ionic with appreciable covalent woof. This conclusions is further supported by the findings from the Born-effective-charge analysis (see below).

Everybody agrees that the number of electrons at a given atomic site is the key quantity for evaluation of the valence state. The accumulated charges inside the appropriately chosen atomic sphere are 18.11, 24.97, 24.76, and 7.16 (all in units of e) for Ca, Co1°, Co2°, and O, respectively. Since there are ambiguities associated with the definition of the boundary of an atomic sphere and no clear-cut distinction between cationic and anionic charges, we turned our attention to the “atom-in-molecule” approach introduced by Bader. Bader gave an elegant approach to this problem with his “interatomic surface” [48] concept, according to which the space in a solid is divided into regions established by surfaces that run through minima in the charge density. A given region is chosen such that at any location on the bordering surface the gradient of the charge density has no component normal to the surface. A region enclosed by such boundary surfaces is referred to as a Bader region. Each Bader region normally contains only one nucleus. By integrating the charge density within the Bader region where a given nucleus is located, and adding electronic charges in

FIG. 5: (Color online) Calculated (a) charge density, (b) charge transfer, and (c) electron-localization function for Ca$_3$Co$_2$O$_6$. The illustrations refer to the (110) plane.
“naturally associated neighboring regions” that do not include a nucleus, the total excess charge on the atom at a given site can be estimated and this charge is named as Bader charge. The advantage of this method is that the analysis is based solely on the charge density, so it is rather insensitive to the basis set used. The Bader charge difference ($\Delta q_B$ relative to the corresponding neutral atom) at each atomic site in Ca$_3$Co$_2$O$_6$ are listed in Table I together with values for the reference substances CoO and LaCoO$_3$. The Bader charge differences for CoO and LaCoO$_3$ give much smaller valence states than the expected values according to a pure ionic model, but provide correct qualitative measures for the transfer of electrons from one site to another.

The Born-effective charge gives information about how much electrons are polarized on application of an electric field. If ions behaves like closed-shell ions, they should carry an effective charge close to their nominal ionic value. On the contrary, a large amount of non-rigid delocalized charge will flow across the skeleton of a compound with covalent directed bonds when the lattice is subjected to displacement [49, 50]. Owing to this covalence effect, one usually obtains larger Born-effective charges than the nominal ionic values. So, one can consider the Born-effective charge as an upper limit for the valence in a given system. The Born-effective charge is indeed a macroscopic concept [51, 52], which involves the polarization of the valence electrons as a whole, while the charge “associated with” a given atom is an ill-defined concept. High Born-effective-charge values indicate that the relative displacements of neighboring ions against each other trigger highly polarized electrons. Roughly speaking, a large amount of delocalized charge is responsible for higher values for the Born-effective charge than the nominal ionic values. As the Born-effective charge concept gives more reasonable values for the valence of the Co atoms in well known systems than the Bader-charge approach, it seemed worthwhile to attempt to use this tool to resolve the valence situation for Co in Ca$_3$Co$_2$O$_6$. The average value of the Born-effective charge (see Table I) for Co in CoO and LaCoO$_3$ is 2.17 and 3.35, respectively, and are reasonably close to the respective formal valence of two and three.

The calculated Born-effective charge for Ca$_3$Co$_2$O$_6$ (Table I) once again confirm that both Ca and Co donate electrons and O accepts electrons in accordance with the traditional ionic picture. However, for a pure ionic system one expects more isotropic values for the Born-effective charges than that obtained for Ca$_3$Co$_2$O$_6$. Considerable anisotropy in the diagonal components of the Born-effective-charge tensor (Table I) along with the noticeable off-diagonal components at the O sites confirm the presence of covalent bonding between oxygen and the neighboring Co atoms. Our other chemical-bonding-analysis tools discussed above also show that there is considerable covalent bonding between Ca and O. Born-effective-charge analyses account for the anomalous contributions (defined as the excess charge relative to the accepted value for the ion in question) to the effective charges. The almost equal value of the $xz$ and $yy$ components of the Born-effective charge at the Co sites reflects the one-dimensional character of the atomic arrangement. The average value of the diagonal components of the Born-effective charge for Ca, Co1, Co2, and O are 2.637, 1.800, 2.269, and −2.01, respectively, indicating that the average valence state of Co$^{1+}$ and Co$^{2+}$ are similar. It is interesting to note that the Bader charges at Co$^{1+}$ and Co$^{2+}$ are in fact almost equal. On the other hand, the $zz$ component (along the chain) of the Born-effective charge at Co$^{1+}$ and Co$^{2+}$ are appreciably different (2.8 vs 4.2) indicating that the nature of the valence state of the two sites are indeed different. However, because of the appreciable degree of covalence in the Co-to-O bonding, the ionic-based valence count for both Co sites comes out much smaller than the expected formal valence of 3+ for Co in Ca$_3$Co$_2$O$_6$.

IV. CONCLUSION

In conclusion, the large difference in the magnetic moment between the Co atoms is due to different degree of covalent character between Co and the surrounding oxygen. The Co$^{1+}$ and Co$^{2+}$ atoms are not in conventional 3+LS and 3+HS state, respectively. Our detailed analyses show that the actual valence states are much smaller than three. We maintain that formal valence concept works well for insulators with pure ionic bonding. If the material under consideration has finite degree of covalent character along with the ionic, the simple ionic picture can not be used to predict the valence states correctly. Our Born-effective-charge analyses suggest that in low-dimensional phases like Ca$_3$Co$_2$O$_6$ the valence electrons are distributed highly anisotropically. As a consequence, the simple formal valence picture can not be used to describe the electronic structure and magnetic properties properly.

V. ACKNOWLEDGEMENT

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TABLE I: Calculated Bader charge difference ($\Delta q_{\text{B}}$; see text) and Born effective charge tensor ($Z_{ij}^\ast$) for non-magnetic Ca$_3$Co$_2$O$_6$, LaCoO$_3$ and antiferromagnetic CoO

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