PHYSICAL REVIEW B **77**, 073102 (2008)

Origin of the light green color and electronic ground state of $LaCrO_3$

Khuong P. Ong,[1] Peter Blaha,[2] and Ping Wu[1,*]
[1]*Institute of High Performance Computing, 1 Science Park Road, #01-01 The Capricorn, Singapore Science Park II, Singapore 117528, Singapore*
[2]*Institute of Materials Chemistry, Vienna University of Technology, Getreidemarkt 9/165, A-1060 Vienna, Austria*

(Received 14 January 2008; published 6 February 2008)

The electronic structure and optical properties of $LaCrO_3$ have been calculated and the origin of the light green color of $LaCrO_3$ has been identified. An optical gap of $\Delta_1 = 3.4$ eV was reproduced in agreement with experiment, which is a charge transfer gap. Another optical gap, $\Delta_0 = 2.15$ eV, which is not present in experiments has also been found and explains the light green color of this compound. The energy band gap between the top of the valence band and the bottom of the conduction band is $\Delta = 1.40$ eV and has Mott character. Our calculated x-ray photoemission spectra (XPS) and x-ray absorption spectra at the oxygen *K* edge (O-*K* XAS) are in very good agreement with experiments. In contrast to previous reports, these results have been obtained using standard generalized gradient approximation calculations, while additional correlation effects for Cr 3*d* states due to an effective Hubbard *U* would result in a colorless $LaCrO_3$ and a disagreement with XPS and XAS experiments. Thus, $LaCrO_3$ should not be considered as highly correlated transition metal oxide, a conclusion also valid for many Cr^{3+} compounds.

DOI: 10.1103/PhysRevB.77.073102 PACS number(s): 78.40.−q, 71.15.Mb, 71.20.Nr, 78.70.Dm

Nowadays, clean energy sources such as fuel cells and their relevant new materials for electrodes or solid electrolytes are chased after due to increasing environmental concerns. Lanthanum chromite oxide, $LaCrO_3$, and $LaCrO_3$-based materials have been considered as excellent candidates for this purpose and may eventually outperform presently used solid electrolytes. Understanding the physical properties and the electronic structure of $LaCrO_3$ is therefore of vital importance in the design of $LaCrO_3$-based materials having good electrochemical properties and leading eventually to an important application. Lanthanum chromite oxide has been reported to be a wide band gap semiconductor with an optical band gap of 3.4 eV,[1,2] which is considered to be a charge transfer gap.[1,2] The origin of this optical band gap is unclear from a theoretical point of view because standard calculations based on density functional theory (DFT) usually obtain much smaller gaps. Various calculations[3–6] based on the local spin-density approximation (LSDA) or the generalized gradient approximation (GGA) yield energy band gaps between 0.6 and 1.45 eV, depending not only in the functional but also, in particular, on the approximations made in solving the Kohn-Sham equations such as the atomic sphere approximation in linear muffin-tin orbital (LMTO) calculations. These calculations yield a gap between the occupied Cr t_{2g} and the unoccupied Cr e_g states. For those reasons and in analogy with other transition metal oxides, also $LaCrO_3$ has been classified as highly correlated oxide and various LSDA+*U* calculations[4,5] have been performed establishing the charge transfer character of the gap. However, almost independent of the value of the Hubbard-*U* parameter, fairly small gaps between 1.2 (Ref. 5) and 2.6 eV (Ref. 4) have been obtained. On the other hand, Hartree-Fork calculations[7] yield an energy band gap which is too large (4.5 eV) and has Mott-Hubbard character.

Thus, we notice that none of existing calculations can explain the experimental optical gap of 3.40 eV, which was obtained from reflectivity data by using the Kramers-Kronig relations. In these "indirect" measurements, the optical conductivity[1,2] and reflectivity spectra[2] of $LaCrO_3$ show no features in the visible range making $LaCrO_3$ obviously a colorless material, which is in strong contradiction to the observed light green color of pure $LaCrO_3$. Because of this, the reported optical conductivity spectrum in the visible range and the nature of 3.40 eV optical gap should be taken with care.

The purpose of this Brief Report is to understand the electronic structure, the optical band gap, and the origin of the light green color of pure $LaCrO_3$, as well as the change of color from green to yellow brownish in case of La and O deficiencies, as reported by experiment. We will demonstrate that $LaCrO_3$ and also many Cr^{3+} compounds do not necessarily belong to the class of highly correlated oxides, and the role of on-site electron correlations due to a strong Hubbard interaction will be discussed. The nature of the 3.40 eV gap will be investigated and we will show that it is related to transitions between the O 2*p* valence band and the bottom of the conduction band. All calculations in this work were carried out with the WIEN2K software package.[8] This program allows to compute the electronic structure of $LaCrO_3$ within DFT utilizing the full-potential (linear) augmented plane wave+local orbital method and applying the Perdew-Burke-Ernzerhof (PBE)-GGA.[9] Eventually, we also used, for comparison with GGA results, the GGA+*U* approach in the fully localized limit with effective *U* parameters. For the atomic sphere radii, we chose values of 2.0, 1.9, and 1.7 a.u. for La, Cr, and O, respectively. Inside the atomic spheres, the partial waves were expanded up to $l_{max} = 10$ and the number of plane waves was limited by a cutoff $R_{MT}K_{max} = 7.0$. The charge density was Fourier expanded with $G_{max} = 14$ Ry. A *k* mesh of 500 *k* points in the full Brillouin zone was used. In addition to the usual valence states, also extra local orbitals for "semicore" states (La 4*d*, 5*s*, 5*p*; Cr 3*s*, 3*p*; and O 2*s*) were added and considered as band states. The optical properties of $LaCrO_3$ have been calculated using the optical package of WIEN2K[10] and the O-*K* edge calculations include the dipole matrix elements between the 1*s* core and the conduction band states.

In our calculations, the structure (space group *Pnma*) and lattice constants of Ref. 11 have been used and the internal structural parameters are relaxed using the PBE-GGA. The relaxed atomic positions are La (0.0267, 0.25, −0.0040), Cr (0, 0, 0.5), O(1) (0.4905, 0.25, 0.0684), and O(2) (0.2193, 0.5361, 0.2195). The good agreement, in particular, for the O positions with neutron diffraction data (Table 3 of Refs. 11 and 12) is an indication that standard GGA is sufficient to describe the distorted Cr-O polyhedron, while in strongly correlated materials such as, e.g., $KCuF_3$, the structural distortions cannot be described without LDA+U.[13] We have also investigated the magnetic order and found a *G*-type antiferromagnetic (AFM) state as the most stable magnetic structure in comparison with ferromagnetic (9.1 mRy/f.u.), A-(−5.7 mRy/f.u.), and C-(−6.9 mRy/f.u.) type AFM orderings. A magnetic moment of Cr of $2.56\mu_B$ [using an enlarged sphere of $R_{\mathrm{MT}}(\mathrm{Cr})=2.3$ a.u.] has been obtained, which is in good agreement with the experimental reports of 2.49 (Ref. 12) or $2.8\mu_B \pm 0.2\mu_B$.[14] Applying LDA+U will increase the magnetic moment, but it will not be larger than $3\mu_B$ in contrast to the reports by Yang *et al.*[5]

In order to get further insight into the electronic structure of $LaCrO_3$, the theoretical (total and partial) density of states (DOS) has been compared with experimental x-ray photoemission spectra (XPS)[15] [see Fig. 1(a)]. The theoretical DOS is shifted by 1.45 eV to align the main major peak (peak A) with the experimental XPS. The *shift* is not to correct the underestimation of the band gap in the local density approximation as discuss by Sharma *et al.* in Ref. 15, but it was indeed applied due to the fact that (i) in experiment, one takes the energy zero as the "middle of the gap," while in theory, we take it at the valence band maximum; and (ii) for insulators, one could have a "homogeneous charging"—problem in experiment which will shift the entire spectrum rigidly without any distortion of broadening and does not change the relative positions of various spectroscopic features.[16] In contrast to Ref. 15 where the theoretical peak C is 0.9 eV higher than the experimental data, our results show very good agreement with experimental XPS. This emphasizes the importance of full-potential calculations, and we conclude that peak C (at −1.5 eV) is mainly due to Cr-up *d*-t_{2g} states, peak A (at −6.0 eV) arises from bonding Cr *d* and O *p*, and peak B (at −4.5 eV) is mainly due to the nonbonding O *p* states. Taking into account an additional effective Hubbard interaction for treating the on-site correlations of Cr 3*d* electrons by using the GGA+U method, e.g., with $U_{\mathrm{eff}}=0.2$ Ry, will shift the Cr-dn and O peaks upward while the Cr-up peak will be shifted downward leading to a large discrepancy between the shape of the theoretical DOS and the experimental XPS [see Fig. 1(a)]. At higher values of U_{eff}($U_{\mathrm{eff}}>0.4$ Ry), peak C will completely disappear and peak B will be higher than peak A due to a superposition of Cr-up *d*-t_{2g} and O *p* contributions. In summary, with increasing U_{eff}, the calculated XPS spectra are quite different from experiment, peak A gets reduced, peak C completely vanishes, and peak B is enhanced and shifted [see Fig. 1(a)]. The theoretical oxygen-*K* edge x-ray absorption spectrum of $LaCrO_3$ [see Fig. 1(b)] shows good agreement with experiments[15] but strongly disagrees with their LMTO calculations,[15] indicating again that one should perform accurate calculations before strong correlation effects are considered to be important. Applying an on-site electron correlation *U* for the Cr 3*d* electrons will result in a reduction of the energy difference between peaks E and D and E and F [see Fig. 1(b)], which is not in agreement with experiment.

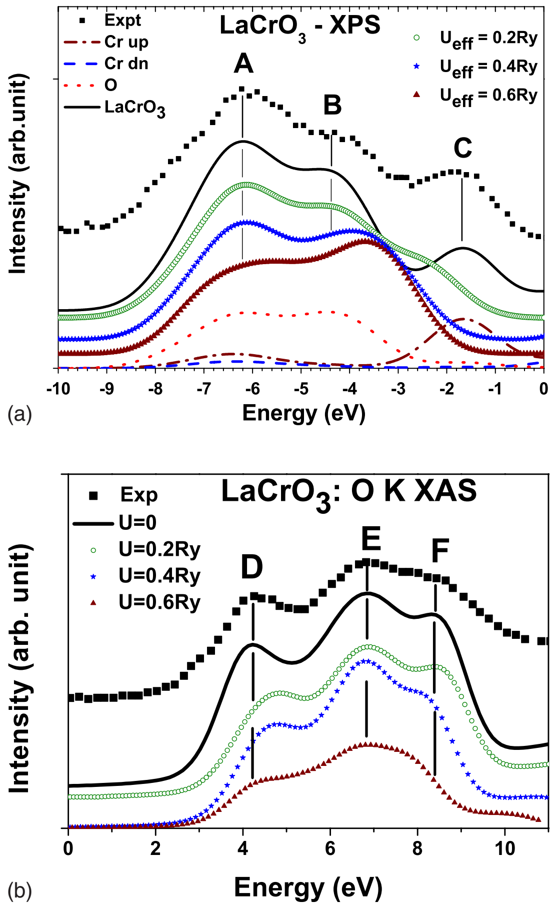

FIG. 1. (Color online) Comparison of the (a) theoretical density of states and (b) x-ray absorption spectra of the oxygen *K* edge (O-*K* XAS) of *G*-type AFM $LaCrO_3$ with experimental XPS and O-*K* XAS spectra (Ref. 15) (squares). The solid, dotted, dashed, and dash-dot-dotted lines represent the total as well as the partial O, Cr up, and Cr dn DOSs of $LaCrO_3$, respectively. The green hollow circle line, the blue star line, and the dark-red up triangle line represent GGA+U calculations with $U_{\mathrm{eff}}=0.2$, 0.4, and 0.6 Ry, respectively. All theoretical curves are broadened with a Gaussian of $\gamma=0.05$ Ry.

The density of states of $LaCrO_3$ is shown in Fig. 2. An energy band gap $\Delta=1.40$ eV, which is the energy gap between the occupied t_{2g} (Cr $d_{x^2-y^2}$, d_{xz}, and d_{yz}) and unoccupied e_g (Cr d_{z^2} and d_{xy}) orbitals, has been obtained. It is a *Mott-type insulating gap*. (We notice here that due to the particular coordinate system, the Cr $d_{x^2-y^2}$ orbital and not the Cr d_{xy} orbital belongs to the t_{2g} states.) The DOS of $LaCrO_3$ reveals also another important transition at $\Delta_1=3.40$ eV, which is the energy gap between the top of the O *p* bands (at −2.0 eV) and the bottom of the Cr e_g conduction bands

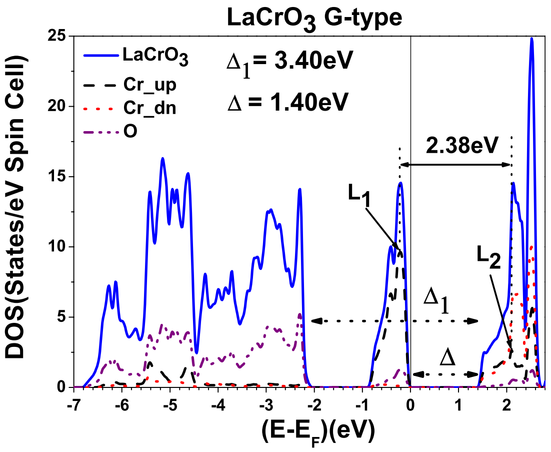

FIG. 2. (Color online) DOS of G-type AFM LaCrO$_3$. The minimum energy band gap $\Delta = 1.40$ eV is the gap between Cr t_{2g} and e_g orbitals (see text). The other gap $\Delta_1 = 3.40$ eV is the optical band gap reported from experiment (Refs. 1 and 2). The green color of LaCrO$_3$ is mainly due to transitions between Cr t_{2g} states near L_1 (-0.23 eV) and Cr e_g bands at L_2 (2.15 eV), and $\Delta(L_1 - L_2) = 2.38$ eV.

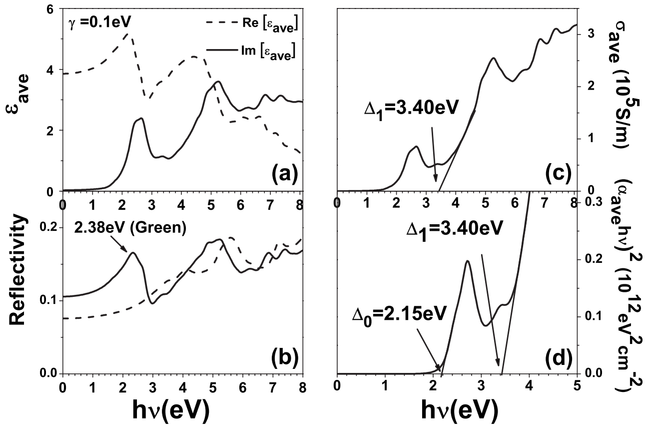

FIG. 3. (a) Average dielectric constant of LaCrO$_3$, $\varepsilon_{av} = (\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz})/3$. (b) Average reflectivity of LaCrO$_3$; the peak at 2.38 eV (0.5025 μm) corresponds to the green color. The dashed line is the reflectivity with $U = 0.2$ Ry which is flat in the visible range resulting in colorless LaCrO$_3$. (c) Average optical conductivity, $\sigma_{av} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, of LaCrO$_3$. (d) $(\alpha_{av} h\nu)^2$ spectrum of LaCrO$_3$ with $\alpha_{av} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$. The gap $\Delta_1 = 3.40$ eV is the optical gap reported in Refs. 1 and 2, while the other optical gap $\Delta_0 = 2.15$ eV was not reported.

(at 1.40 eV) (see Fig. 2). This constitutes a *charge transfer gap*. As we will indicate in the calculation of optical properties, the charge transfer gap $\Delta_1 = 3.40$ eV is indeed the optical gap of 3.40 eV reported experimentally,[1,2] while the optical transitions between Cr t_{2g} and e_g will lead to the green color of LaCrO$_3$. These transitions, however, result in weak optical absorptions. So far, the experimental optical gap, 3.40 eV, was considered as the energy band gap between the top of the valence band and the bottom of the conduction band by previous theoretical works.[3–5] In order to obtain such an energy band gap, the Hubbard interaction U for treating electron correlations of Cr $3d$ electrons was introduced and LaCrO$_3$ was considered as highly correlated oxide in analogy to similar LaMO$_3$ compounds. As mentioned in Introduction, the energy gap of 3.40 eV was reported based on reflectivity data, but pure LaCrO$_3$ has a light green color and thus must have a gap in the visible range.

The optical transitions are not only determined by the DOS, and dipole transition matrix elements may play an important role. We have also calculated the optical constants directly, and Fig. 3(a) shows the imaginary and real parts of the dielectric function ε. The imaginary part ε_2 shows the expected onset near 1.5 eV and a pronounced peak between 2 and 3 eV stemming forms "Mott" transitions, while the stronger features above 4 eV are due to charge transfer excitations.

In contrast to the experimental report on the reflectivity of LaCrO$_3$ (Ref. 2) (where the reflectivity is flat or colorless in the visible range), the calculated average reflectivity, $R_{av} = (R_{xx} + R_{yy} + R_{zz})/3$, of the LaCrO$_3$ compound [see Fig. 3(b)] reveals a clear peak at 2.38 eV ($\sim$502 nm, wavelength of green light). This peak comes from optical transitions between the Cr t_{2g} and Cr e_g bands (which are, of course, partly hybridized with O p). These transitions are in the visible range and reflect the color of LaCrO$_3$. Our calculation reveals that the green color of LaCrO$_3$ has its origin from the transition between Cr t_{2g} bands centered at L_1 (-0.23 eV) and Cr e_g bands at L_2 (2.15 eV) (see Fig. 2). We believe that the 2.38 eV peak should be observed in reflectivity measurement of pure LaCrO$_3$. Recently, an experiment on the reflectivity of La$_{1-y}$CrO$_3$ ($y \sim 3\% - 5\%$) (Ref. 17) reveals peaks at 1.6 and 2.26 eV in the reflectivity curve which reflects exactly the yellow brownish color of nonstoichiometric La$_{1-y}$CrO$_3$. This experiment supports the existence of the 2.38 eV peak in the reflectivity curve of pure LaCrO$_3$ compound because the introduction of La or oxygen deficiency in LaCrO$_3$ results in a reduction of the energy band gap, making the separation between the Cr t_{2g} and Cr e_g bands smaller,[18] and changes the color from green (pure LaCrO$_3$) to yellow brownish (La$_{1-y}$CrO$_3$). The existence of these low energy peaks in the reflectivity of La$_{1-y}$CrO$_3$ supports therefore the existence of the 2.38 eV peak in the reflectivity of pure LaCrO$_3$.

The influence of electron correlations of Cr $3d$ electrons due to the Hubbard interaction on the optical properties of LaCrO$_3$ has also been investigated. We found that applying $U = 0.2$ Ry will flatten the reflectivity curve [see Fig. 3(b)] and reduce the intensity of reflectivity in the visible range. Increasing U makes the reflectivity curve even flatter and reduces its magnitude in the visible range resulting in colorless or transparent LaCrO$_3$ which is not observed.

In order to verify the optical gaps of LaCrO$_3$, an average spectrum of the optical conductivity $\sigma_{av} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$ has been calculated [see Figs. 3(c) and 3(d)]. Two optical gaps have been obtained: $\Delta_0 = 2.15$ eV and $\Delta_1 = 3.4$ eV. The first optical gap, $\Delta_0 = 2.15$ eV, corresponds to the transition between occupied Cr t_{2g} and unoccupied Cr e_g bands and was not found in experiment.[1] It is not surprising since the reported optical conductivity[1,2] was calculated from the reflectivity data via the Kramer-Kronig formula and the experimental reflectivity is transparent in the visible range in this experiment. However, we notice that there is strong evidence of Cr t_{2g} to Cr e_g band transitions in the visible range also in other Cr^{+3} compounds such as in Cr_2O_3 (Ref. 19) (with $\Delta = 169\,38\ cm^{-1} \sim 2.10$ eV) or K_2NaCrF_6 (Ref. 20) (with $\Delta = 161\,00\ cm^{-1} \sim 2.00$ eV), which provide additional support to this prediction. This optical gap is the lowest spin allowed transition between $^4A_{2g}$ and $^4T_{2g}$ crystal field states. The other gap $\Delta_1 = 3.4$ eV is in good agreement with experiment; however, this gap is not the energy gap between the top of the valence band (Cr t_{2g}) and the bottom of the conduction band, but it is the energy gap between the top of the O p bands and the bottom of the Cr e_g conduction bands, as discussed above (see Fig. 2).

Summarizing all results, we find absolutely no evidence for strong correlations of the Cr $3d$ states in $LaCrO_3$. Standard GGA calculations can explain the structural distortions of the Cr-O polyhedron, the magnetic ground state, XPS and O-K x-ray absorption spectra (XAS), the light green color of pure $LaCrO_3$, and the strong optical gap at 3.4 eV found in experiment. Using GGA+U leads to poorer agreement with experiment for practical all investigated properties. Previously, reported results concluded that strong correlations within the Cr $3d$ shell are present, but we demonstrate that it is important to use an accurate electronic structure method and come to the conclusions that this technological important material is a case where "nature minimizes correlation effects" and crystal field effects dominate. These conclusions seem to be valid also for many Cr^{3+} compounds and question the commonly used LDA+U approach for these materials [see, e.g., the calculations for Cr_2O_3 (Ref. 23)] and may be also for some other (early) transition metal compounds, where crystal field effects may dominate local on-site correlations, provided the number of $3d$ electrons is compatible with crystal field symmetry. We suggest new experiments to verify the predicted optical absorption at 2.15 eV.

K.P.O. would like to thank Jacques Plevert for digitalization of experimental data in Fig. 1. Fruitful discussions with J. Plevert and Valeri Litgachev are acknowledged. We would like to thank D. D. Sarma for his help in addressing the experimental homogeneous and/or inhomogeneous charging problem. This work was sponsored by Agency for Science, Technology And Research of Singapore (A*STAR) under SERC Grant No. 042 101 0081.

---

*Corresponding author. wuping@ihpc.a-star.edu.sg

[1] T. Arima, Y. Tokura, and J. B. Torrance, Phys. Rev. B **48**, 17006 (1993).

[2] T. Arima and Y. Tokura, J. Phys. Soc. Jpn. **64**, 2488 (1995).

[3] N. Hamada, H. Sawada, and K. Terakura, *Spectroscopy of Mott Insulators and Correlated Metals* (Springer-Verlag, Berlin, 1995), p. 95.

[4] I. Solovyev, N. Hamada, and K. Terakura, Phys. Rev. B **53**, 7158 (1996).

[5] Z. Yang, Z. Huang, L. Ye, and X. Xie, Phys. Rev. B **60**, 15674 (1999).

[6] R. Ravindran, R. Vidya, H. Fjellvag, and A. Kjekshus, J. Cryst. Growth **268**, 554 (2004).

[7] T. Mizokawa and A. Fujimori, Phys. Rev. B **54**, 5368 (1996).

[8] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave+Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, TU Vienna, Austria, 2001).

[9] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[10] R. Abt, C. Ambrosch-Draxl, and P. Knoll, Physica B **194-196**, 1451 (1994); C. Ambrosch-Draxl and J. Sofo, Comput. Phys. Commun. **175**, 1 (2006).

[11] G. Li, X. Kuang, S. Tian, F. Liao, X. Jing, Y. Uesu, and K. Kohn, J. Solid State Chem. **165**, 381 (2002).

[12] N. Sakai, H. Fjellvag, and B. C. Hauback, J. Solid State Chem. **121**, 202 (1996).

[13] V. Anisomov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys.: Condens. Matter **9**, 767 (1997).

[14] W. C. Koehler and E. O. Wollan, J. Phys. Chem. Solids **2**, 100 (1957).

[15] D. D. Sarma, N. Shanthi, and P. Mahadevan, Phys. Rev. B **54**, 1622 (1996).

[16] There is no excessive inhomogeneous charging problem in the $LaCrO_3$ sample which may lead to a distorted spectrum [D. D. Sarma (private communication)].

[17] M. N. Iliev, A. P. Litvinchuk, V. G. Hadjiev, Y.-Q. Wang, J. Cmaidalka, R.-L. Meng, Y.-Y. Sun, N. Kolev, and M. V. Abrashev, Phys. Rev. B **74**, 214301 (2006).

[18] Khuong P. Ong, P. Wu, L. Lu, and S. P. Jiang, Appl. Phys. Lett. **90**, 044109 (2007).

[19] The dark green Cr_2O_3 compound has the same color center Cr^{3+} and similar features of the electronic structures as $LaCrO_3$. From experimental data (Ref. 21) and using the Taneba-Sugano diagram (Ref. 22), an energy gap (from $^4A_{2g}$ state to $^4T_{2g}$ state) of $16\,938\ cm^{-1} \sim 2.10$ eV for the lowest spin allowed transition has been obtained, which is nearly the same as the 2.15 eV gap that we calculated for $LaCrO_3$. Therefore, the 2.15 eV gap of $LaCrO_3$ matches the transition between $^4A_{2g}$ state and $^4T_{2g}$ state.

[20] D. L. Wood, J. Ferguson, K. Knox, and J. F. Dillon, Jr., J. Chem. Phys. **39**, 890 (1963).

[21] S. I. Shablaev, I. B. Areshev, and R. V. Pisarev, Fiz. Tverd. Tela (S.-Peterburg) **42**, 1821 (2000).

[22] S. Sugano and Y. Tanabe, J. Phys. Soc. Jpn. **13**, 880 (1958).

[23] N. J. Mosey and E. A. Carter, Phys. Rev. B **76**, 155123 (2007); A. Rohrbach, J. Hafner, and G. Kresse, *ibid.* **70**, 125426 (2004).