

Charge disproportionation and the pressure-induced insulator–metal transition in cubic perovskite PbCrO_3

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Contributed by John B. Goodenough, December 29, 2014 (sent for review May 8, 2014)

The perovskite PbCrO_3 is an antiferromagnetic insulator. However, the fundamental interactions leading to the insulating state in this single-valent perovskite are unclear. Moreover, the origin of the unprecedented volume drop observed at a modest pressure of $P = 1.6$ GPa remains an outstanding problem. We report a variety of *in situ* pressure measurements including electron transport properties, X-ray absorption spectrum, and crystal structure study by X-ray and neutron diffraction. These studies reveal key information leading to the elucidation of the physics behind the insulating state and the pressure-induced transition. We argue that a charge disproportionation $3\text{Cr}^{4+} \rightarrow 2\text{Cr}^{3+} + \text{Cr}^{6+}$ in association with the 6s-p hybridization on the Pb^{2+} is responsible for the insulating ground state of PbCrO_3 at ambient pressure and the charge disproportionation phase is suppressed under pressure to give rise to a metallic phase at high pressure. The model is well supported by density function theory plus the correlation energy U (DFT+ U) calculations.

high pressure | perovskite | insulator–metal transition | charge disproportionation

Electron–electron correlations can open up a gap near the Fermi energy in a partially filled band system to give rise to a Mott insulator without changing the translation symmetry (1). However, how to justify the insulating ground state in the cubic perovskite PbCrO_3 with a 2/3-filled band remains controversial (2–11). An unphysically large U needs to be used in the density function theory (DFT) calculation (10) to open a gap, indicating that electron–electron correlations alone is insufficient to account for the insulator phase. More surprisingly, the structure undergoes a first-order transition at $P = 1.6$ GPa to another cubic phase with an extremely large volume drop (6). To clarify the fundamental interactions leading to the cubic insulating state and whether the pressure-induced volume collapse is accompanied with an insulator–metal transition, we carried out a suite of high-pressure experiments including structural characterization, measurements of resistivity, and X-ray absorption near edge structure (XANES) under high pressure and performed DFT with Hubbard U correction (DFT+ U) calculations. Detailed information about the experiments, the DFT calculation, and the simulation for XANES is provided in *SI Text*.

The PbCrO_3 perovskite was known to be stabilized under high pressure and high temperature (HPHT) in the 1960s (2). Structural studies by X-ray and neutron diffraction revealed that it crystallizes as a cubic $Pm\bar{3}m$ perovskite with a lattice constant of $a_0 \sim 4.00$ Å and exhibits a type G antiferromagnetic (AFM) order below $T_N = 240$ K in contrast to the type C AFM order of CaCrO_3 below $T_N = 90$ K and that of the tetragonal phase of SrCrO_3 . The magnetic moment on Cr^{4+} as refined from neutron diffraction is $1.9 \mu_B$, which is very close to the spin-only moment of $2 \mu_B$ expected for localized d^2 electrons. In comparison with other Cr^{4+} -containing perovskites, ACrO_3 ($A = \text{Ca}, \text{Sr}$) (9, 12),

PbCrO_3 exhibits peculiar structural and physical properties. The unit-cell volume V_0 of PbCrO_3 is significantly larger than expected based on the A cation size r_A (13) in the $\text{A}^{2+}\text{Cr}^{4+}\text{O}_3$ family and the prediction with the software SPuDs (14). PbCrO_3 also shows a much higher resistivity and activation energy E_a than those found in CaCrO_3 and SrCrO_3 (9). These peculiarities of PbCrO_3 may be attributed to the stereochemical effect of the Pb 6s² lone-pair electrons, but this effect normally reduces the symmetry from cubic. A comparative study of the electron energy loss spectroscopy (EELS) of ACrO_3 ($A = \text{Ca}, \text{Sr}, \text{Pb}$) perovskites by Arévalo-López et al. (4) has indeed shown a subtle difference in the O-K edge spectra as a result of different A–O interactions. In the calculation by Ganesh and Cohen (7), the peculiar electronic configuration on Pb^{2+} makes Pb off-centering energetically favorable to form a tetragonal structure at ambient pressure as occurs in PbTiO_3 . High pressure favors the cubic phase by suppressing the Pb off-centering displacement. However, the metallic phase predicted with this model does not match the experimental result for the phase at ambient condition. Moreover, a tetragonal phase is not confirmed by experiments.

Results and Discussion

In addition to an unusually large cell volume, PbCrO_3 is well known to have a highly irregular peak profile in the X-ray diffraction (XRD) pattern (3). This observation motivates us to

Significance

The steric activity of the lone pair electrons of Pb^{2+} -containing compounds distorts the crystal structure and produces exotic physical properties. In ferroelectric PbTiO_3 and PbVO_3 , the lone-pair electrons hybridizing with the oxygen lead to polarized MO_6 octahedra. In PbRuO_3 , the hybridization induces unprecedented Pb–Ru bonds at high pressure. The stereochemical effect in PbCrO_3 makes Pb bond with oxygen without a long-range periodicity. Under the influence of displaced Pb^{2+} , Cr^{4+} undergoes a charge disproportionation that opens up a gap. In contrast to the pressure effect on PbTiO_3 and PbRuO_3 , pressure restores the undistorted perovskite structure in PbCrO_3 . This result implies that the stereochemical effect of Pb^{2+} in a perovskite depends sensitively on the number and energy of the d electrons.

Author contributions: J.C., J.B.G., and J.-S.Z. designed research; J.C., K.E.K., S.A.L., Y.D., Y.S., L.G.M., Z.-Y.L., X.L., A.M.d.S., M.R.S., G.S.H., and J.-S.Z. performed research; K.M. and Y.U. contributed new reagents/analytic tools; K.E.K., S.A.L., Y.D., G.S.H., and J.-S.Z. analyzed data; and J.C., S.A.L., G.S.H., J.B.G., and J.-S.Z. wrote the paper.

The authors declare no conflict of interest.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1424431112/-DCSupplemental.

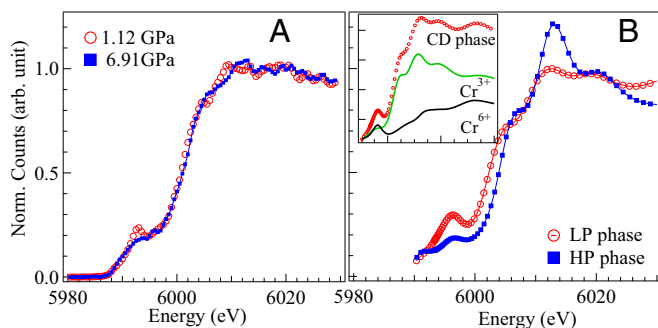


Fig. 3. (A) The XANES data of PbCrO_3 under two pressures, one on each side of P_c . (B) Calculated XANES with the CD model for the LP phase and the simple cubic structure for the HP phase. *Inset in B* shows contributions from Cr^{3+} and Cr^{6+} in the XANES calculation for the CD model.

In addition to measuring bulk properties of PbCrO_3 under pressure, we used Cr $K\alpha$ PYF XANES as a microscopic probe to investigate directly the electronic structure change on crossing the transition. The PYF XANES of the Cr–K edge was collected at 1.12 and 6.91 GPa and is displayed in Fig. 3A. The pre-edge feature reflects the information of the empty 3d band structure above the Fermi energy, whereas the feature at the shoulder of the spectrum is mainly related to the empty Cr 4p band. The most obvious change between the low-pressure (LP) phase and the high-pressure (HP) phase is a diminishing of the hump at the pre-edge in the HP phase. Our calculations below explain well these changes in XANES by the insulator-metal transition and the structural change.

In the second half of this paper, we report our DFT+U calculations. In the HP cubic phase ($Pm\bar{3}m$), each Cr^{4+} ion must be located at an octahedral site with six equivalent Cr–O bonds, as required by the space group in Fig. 4A. Fig. 4B shows the electron density of states (DOSs) projected on the atomic orbitals of PbCrO_3 ; the threefold-degenerate $\text{Cr } t_{2g}$ states are partially filled with two electrons, whereas the doubly degenerated $\text{Cr } e_g$ states are completely empty. For $U_{\text{eff}} = 2.13$ eV used in our calculations, a clear exchange splitting means that a ferromagnetic state is more stable than an antiferromagnetic state*; the energy difference between the ferromagnetic and antiferromagnetic states is directly related to the U_{eff} value. A 1/3-filled metallic band is near the crossover from ferromagnetic coupling for a 1/4-filled band and antiferromagnetic ordering for a half-filled band. A metallic state as indicated by the band structure from our DFT calculations is consistent with experimental results. Our generalized gradient approximation (GGA)+U calculations also predict the lattice constant a and the bulk modulus B_0 to be 3.906 Å and 162.6 GPa, respectively, in agreement with the experimental values of $a = 3.862$ Å and $B_0 = 187$ GPa by Xiao et al. (6). The slight overestimation of a is due to the well-known underbinding tendency in the GGA calculation. A smaller $B_0 = 98 \pm 3$ GPa from the Birch-Murnaghan (BM) fitting in Fig. 24 can be attributed to a relatively narrow pressure range for this fit.

Now we turn to the cubic phase of PbCrO_3 at ambient pressure. Following the experimental observation, we first let the cell volume expand by 10% based on the HP cubic phase and search for local structural configurations with lower energy. We found that the cell volume expansion leads to significant atomic displacements from the ideal cubic positions; Cr^{4+} tends to undergo a charge disproportionation to $\text{Cr}^{+(4+\delta)}$ and $\text{Cr}^{+(4-\delta)}$. For a quantitative description of the CD phase, we constructed two model

systems that consist of two and three PbCrO_3 formula units (f.u.), which can allow the $2 \times 4^+ \rightarrow 3^+ + 5^+$ and $3 \times 4^+ \rightarrow 3^+ + 3^+ + 6^+$. As illustrated in Fig. 5A, the equilibrium volume for the CD configuration $3^+ + 3^+ + 6^+$ is predicted to be $65.2 \text{ Å}^3/\text{f.u.}$, which is about 9% greater than $59.6 \text{ Å}^3/\text{f.u.}$ for the HP cubic structure. The bulk modulus B_0 for the CD phase is calculated to be 78.2 GPa, which is close to the experimental value $B_0 = 68 \pm 3$ GPa in Fig. 24. On the other hand, the $3^+ + 5^+$ configuration tends to be rather unstable and thus returns to the HP cubic structure on volume relaxation. However, we should point out that the energy difference between the $3^+ + 5^+$ and $3^+ + 3^+ + 6^+$ model structures is insignificant (~ 0.06 eV/f.u. at a fixed volume of 64.7 Å^3); this may imply that, at elevated temperatures, Cr^{5+} would possibly coexist with prevailing Cr^{3+} and Cr^{6+} .

In an optimized model structure with the $3^+ + 3^+ + 6^+$ configuration shown in Fig. 5B, Pb atoms are displaced substantially toward Cr^{3+} atoms (which also deviate slightly from the ideal cubic positions). The average displacements of Pb and Cr atoms with respect to the cubic lattice are predicted to be 0.37 and 0.20 Å, respectively; those displacements could provide an explanation for the observed irregular profile of the XRD peaks. The Cr^{3+} and Cr^{6+} are found to be octahedrally and tetrahedrally coordinated, respectively, by O anions, yielding CrO_6 octahedra and highly distorted CrO_4 tetrahedra by random displacements of the Cr^{6+} within an octahedral site as indicated in Fig. 5B. In a distorted CrO_4 tetrahedron, there are two short Cr–O bonds (with double bond Cr=O character) and two relatively long bonds (with single bond Cr–O character); the respective bond distances of 1.65 and 1.78 Å are comparable to 1.59 and 1.78 Å for the calculated Cr=O and Cr–O bonds in a tetrahedral $\text{CrO}_2(\text{OH})_2$ cluster in the gas phase. In neighboring Cr^{6+} and Cr^{3+} octahedra, a bridging O anion tends to move toward neighboring Cr^{6+} to give a long Cr–O bond distance of 2.40 Å, whereas the other five Cr–O bonds have bond lengths of 2.00 ± 0.05 Å, which is close to a typical Cr^{3+} –O bond distance of 2.0 Å in RCrO_3 (16). It is also worthwhile to note that the distance from Pb atoms to O atoms (connected to Cr^{3+} atoms) is 2.43–2.56 Å, which is substantially shorter than the 2.85 Å estimated for the ideal cubic case; the shorter Pb–O bonds are indicative of a possible contribution of the Pb–O interaction to stabilizing the CD phase (*vide infra*).

As shown in Fig. 5C, the DOS analysis for the ambient-pressure phase of PbCrO_3 with the $3^+ + 3^+ + 6^+$ configuration clearly demonstrates that the charge disproportionation provokes an energy gap in the $\text{Cr}^{5+}/\text{Cr}^{4+}$ redox band, in contrast to the ideal cubic structure of Fig. 4. The upper valence bands from 0 eV down to -1.2 eV consist mainly of half-filled $\text{Cr}^{3+} t_{2g}$ and O 2p orbitals, whereas the empty t_{2g} orbitals of Cr^{6+} primarily constitute the conduction band minimum. The DOS plot also shows

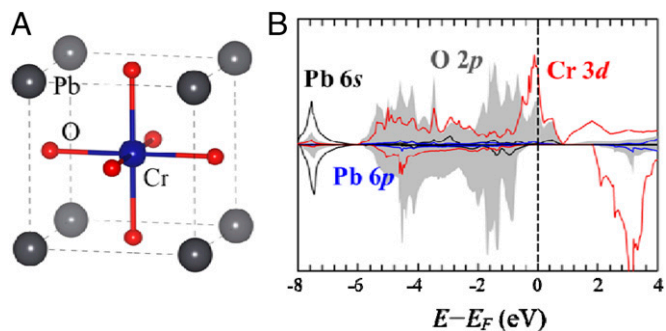


Fig. 4. (A) Schematic drawing of a cubic perovskite structure at $P > P_c$. (B) DOS projected on the atomic orbitals of the HP PbCrO_3 phase; the dash line indicates the position of the Fermi level.

*The relative stability tends to be sensitive to the choice of U_{eff} ; nonetheless, both the ferromagnetic and antiferromagnetic states are predicted to be metallic, which is consistent with experiments.

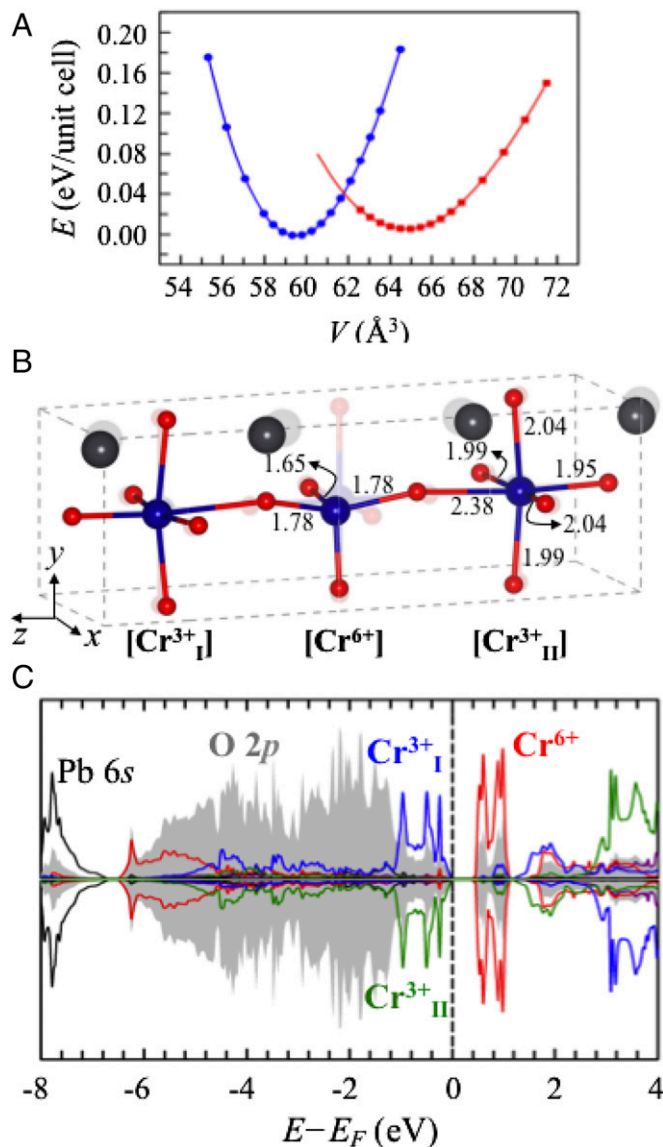


Fig. 5. (A) The relative energies (E) per formula unit (f.u.) for the ideal cubic perovskite (blue) and the CD (red) phases of PbCrO_3 as a function of cell volume (V). (B) The optimized CD model structure with bond length in Angstroms together with the ideal cubic structure shown as faded structure at the background. (C) DOS projected on the Pb6s, O2p, and Cr3d orbitals in the CD model.

that two adjacent Cr^{3+} ions have an overlapping half-filled t^3 orbital to give an antiferromagnetic coupling, which is consistent with the rules for superexchange interactions and the type-G AF ordering observed. The overlap of the Pb $6s, 6p$ and Cr $3d$ energies in the range $E_f - 4.5 \text{ eV} < E < E_f - 1.2 \text{ eV}$ indicates the existence of strong interactions that are manifest as empty antibonding primarily $\text{Cr}^{6+}:3d$ states and filled bonding Pb $6s, 6p$. The Pb–O interactions stabilize the localized $\text{Cr}^{3+}:t^3$ states via the inductive effect to create an energy gap between Cr^{6+} and Cr^{3+} $3d$ states. To confirm the role of Pb in the electronic structure of PbCrO_3 , we also performed the same calculation for isostructural SrCrO_3 . The CD phase with the $3^+ + 3^+ + 6^+$ configuration having half-filled and empty t_{2g} states turns out to be highly unlikely; instead the phase with partially filled Cr t_{2g} orbitals is more stable (Fig. S2). The predicted cubic phase for SrCrO_3 is consistent with the experimental result. Additionally,

we also found that the Cr t_{2g} orbitals become partially filled instead of fully empty or half-filled where the Pb–O interaction is reduced by moving Pb atoms back to the ideal cubic positions (Fig. S3). This analysis highlights that the peculiar electron configuration on Pb and its nuclear position shifting from the position in the ideal cubic structure play important roles in the charge disproportionation of Cr in PbCrO_3 at ambient pressure.

Finally, XANES data provide an important test to our CD model and our picture of the pressure-induced insulator–metal transition. The shape and position of the Cr *K*-edge are well known to be a strong function of Cr valence (17–19). As displayed in Fig. 3*A*, one distinct difference between the two measured XANES spectra is that the LP PbCrO_3 phase exhibits a single intense pre-edge peak, whereas the intensity of the pre-edge peak is significantly reduced for the HP phase. As shown in Fig. 3*B*, the calculated XANES for the CD and the simple cubic phases captures the essential features of the experimental results. The strong absorption peak in the pre-edge region is generally attributed to a quadruple transition of a $1s$ electron to an empty antibonding $3d_{t_{2g}}$ (20). As shown in a decomposed plot of the calculated XANES in the *Inset* of Fig. 3*B*, the pre-edge peak is primarily due to the contribution from Cr^{6+} . However, the same transition is not allowed in a high-symmetry octahedral environment of Cr^{6+} or Cr^{4+} (17–19). It should be stressed that the pattern given in Fig. 5*B* is one of possible CD of PbCrO_3 at ambient pressure.

Summary of Experimental Findings and the DFT Calculation

A combination of new experiments and DFT+U calculations allows us to clarify the nature of the insulator phase and the mechanism of the pressure-induced first-order transition in perovskite PbCrO_3 . In contrast to PbVO_3 in which shortening the distance between Pb^{2+} and V^{4+} to share the lone-pair electrons leads to a tetragonal polar phase, the Pb displacements in PbCrO_3 are distributed around its position in the cubic perovskite structure. Assisted by static disordered Pb-O bonding, a negative-U charge density wave on Cr-O arrays provides an inelastic energy that competes with the electron-electron correlation to give rise to the insulator phase at ambient pressure. The simulated XANES profile based on the charge disproportionation model matches well the experimental data. The cell-volume collapse at $P_c \sim 3$ GPa is due to a first-order localized to itinerant electronic transition as demonstrated by our transport property and XANES under high pressure. The lattice parameter, bulk modulus, and the result of XANES measurement of the metallic phase at high pressure can be well-described by our DFT+U calculations. The predicted ferromagnetic phase at $P > P_c$ remains to be confirmed by experiment.

Materials and Methods

Polycrystalline PbCrO_3 samples used in the present study were obtained by sintering a stoichiometric mixture of PbO and CrO_2 powders at 8 GPa and 800 °C for 30 min with a Walker-type multianvil module. High-resolution diffraction data (SXRD) have been collected in the temperature range of 120–300 K with synchrotron radiation on beamline 11-BM ($\lambda = 0.41396$ Å) at the Advanced Photon Source, Argonne National Laboratory. The obtained SXRD data were analyzed with the Rietveld method by using the General Structure Analysis System (GSAS) program. The high-pressure structural study at room temperature was carried out with a diamond-anvil cell mounted on a four-circle diffractometer with Mo anode. In situ high-pressure neutron diffraction measurements were measured at the SNAP beamline in the Spallation Neutron Source in Oak Ridge National Laboratory. The SNAP instrument is a medium resolution time of flight diffractometer optimized for measurements under high pressure. Temperature dependence of resistivity down to 4.5 K under different hydrostatic pressures up to 8 GPa was measured with the four-probe method in a cubic anvil apparatus. The Cr $K\alpha$ partial fluorescence yield (PFY) X-ray absorption spectrum under pressure was collected at HPCAT-16IDD, Advance Photon Sources of Argonne National Laboratory, using a Panoramic diamond anvil cell.

All calculations reported herein were performed by using DFT with Hubbard U correction (DFT+U) within the GGA-PBE, as implemented in the Vienna Ab-initio Simulation Package (VASP 5.2.2).

Note Added in Proof. While this paper was in press, we have become aware of a report by Wu, et al. (21). The authors have studied the X-ray absorption spectra of PbCrO_3 under pressure; they have reached a similar conclusion that a charge disproportionation occurs in the low-pressure phase of PbCrO_3 .

ACKNOWLEDGMENTS. The Texas Advanced Computing Center is acknowledged for providing HPC resources. This work was supported by the National

Science Foundation (NSF) Materials Interdisciplinary Research Teams (Division of Material Research-1122603) and the Welch Foundation (F-1066 and F-1535). J.C. acknowledges the support of the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant XDB07000000), the Ministry of Science and Technology (MOST) and NSF of China (Grants 2014CB921500 and 11304371), and Japan Society for the Promotion of Science (JSPS) fellowship for foreign researchers (Grant 12F02023). Use of the Advanced Photon Source at Argonne National Laboratory was supported by the US Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357. Research at Spallation Neutron Source in Oak Ridge National Laboratory was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.

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