*B*1-to-*B*2 phase transition of transition-metal monoxide CdO under strong compression

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This paper reports the experimental research on the compressibility and phase transition of CdO up to 176 GPa at room temperature using high-resolution angular-dispersive x-ray diffraction from synchrotron source combined with the diamond anvil cell technique. The phase transition from NaCl (*B*1)- to CsCl (*B*2)-type structure for CdO was observed at pressure about 90.6 GPa, which is uniquely observed in the transition-metal oxide family for the pressure-induced direct *B*1-*B*2 transition and in good agreement with the theoretical prediction. The bulk modulus of the *B*1 and *B*2 phases of CdO at zero pressure was estimated as 147 and 169 GPa, respectively. The 3*d* and 4*d* transition-metal monoxides ZnO and CdO were both predicted to undergo a *B*1-to-*B*2-type structural transformation under high pressure based on first-principles total energy calculations; the difference in the bulk moduli between the results of this experiment and simulations, and the possibility of a similar *B*1-to-*B*2 phase transition in ZnO are discussed.

I. INTRODUCTION

The physical properties of the transition-metal oxides have been extensively studied.[1] The compressibility and phase stability of the oxide under high pressure are one of basic subjects, and high-pressure experiments above magabar (100 GPa) have been performed for some interesting transition-metal oxides, such as FeO, MnO, CoO, and NiO.[2–5] These experimental works have benefited from well-developed static high-pressure techniques and synchrotron-related methods. Meanwhile, current theoretical approaches have been well developed and now have the capability to determine, predict, and understand the structure of chemical compounds. The high-pressure-induced transformation is an active subject in accurate computational researches.[6–8] Recently, the 3*d* and 4*d* transition-metal monoxides ZnO and CdO were predicted to undergo a high-pressure-induced phase transformation from NaCl to CsCl structural type (known, respectively, as *B*1 and *B*2 type) at pressures of about 256 and 89 GPa, respectively.[9,10] These predictions were based on total energy calculations in the framework of density functional theory and were expected to stimulate corresponding high-pressure experimental work. However, the accuracy of the predicted phase transition pressure, which was determined from the overlap of the energy-volume curves of *B*1 and *B*2 phases, is somewhat questionable. The several factors altering such predictions are the relativistic correction, nonzero temperature, and zero-point motion effect not being included in these calculations. Thus, accurate diffraction measurements for CdO were performed in order to check the validity of the theoretically predicted high-pressure phase transition.

CdO has a cubic structure of *B*1 type at ambient conditions. Its structure remains stable up to the melting temperature at room pressure and up to 35 GPa pressure at room temperature from a previous report by Drickamer *et al.*[11] In the first-principles calculations,[9] the potential phases, such as rocksalt, cesium chloride, nickel arsenide, zinc-blende, orthorhombic *cmcm*, cinnabar, and wurtzite structures, were calculated in their equilibrium geometries and curves of the energy-volume (*E-V*) relationship were obtained. The bulk modulus and equilibrium lattice parameter were estimated by fitting the energy as a function of volume according the Murnaghan equation of state (EOS).[12] The phase transition pressure P_{Tc} was estimated from the intersection of the *E-V* curves of *B*1 and *B*2 phases. Correspondingly, the lattice constant a_0 and the bulk modulus B_0 were determined by the shape of the *E-V* curves. Comparison of the calculated a_0 and B_0 with high-quality experimental data is vital to evaluate such simulation results.

II. EXPERIMENT

Two sets of experimental bulk moduli data of the *B*1 phase of CdO were available from the diffraction studies by Drickamer *et al.*[11] (1966) and Zhang[13] (1999) (see Table I for details), respectively. However, there were significant differences between these two sets of data. This causes confusion when comparing them with the calculated values. To clarify the discrepancy between the measured bulk modulus of the *B*1 phase CdO, experiment run No. 1 (Ref. 14) was performed at room temperature for *in situ* high-pressure angle-dispersive x-ray diffraction (ADXRD) at ID-B station of HP-CAT, Advanced Photon Source, Argonne National Laboratory. Polycrystalline cadmium monoxide with a nominal purity of 99.998% (Puratronic, Alfa Aesar) was loaded into the gasket hole between diamond anvils. Methanol-ethanol (4:1) mixture, which could generate quasi-hydrostatic-pressure conditions below 10 GPa, was used as pressure transmitting medium to minimize the uniaxial stress effect. Pressure measurements were based on the ruby fluorescence method.[15] The diffraction patterns were collected by a Mar345 image plate, and the exposure times were typically between 10 s and 2 min. The FIT2D program was used to integrate the image,[16] and the GSAS program was used to structural refinements.[17]

TABLE I. Equation-of-state parameters for CdO at room temperature (XRD, x-ray diffraction; ADXRD, angle-dispersive XRD; EDXRD, energy-dispersive XRD; DAC, diamond anvil cell; DIA, DIA-type large-volume apparatus; DP, Drickamer press; GGA, generalized gradient approximation).

Structural type	B_0 (GPa)	B_0'	Pressure range (GPa)	Pressure marker	Pressure medium	Techniques	Reference
B1	150 ± 1	4 (fixed)	0–9.7	Ruby	Methanol-ethanol	ADXRD/DAC	This work, run 1
	147 ± 4	4.2 ± 0.1	0–89	Au	None	ADXRD/DAC	This work, run 2
	148 ± 1	4 (fixed)	0–8.1	NaCl	BN	EDXRD/DIA	Ref. 13, 1999
	150 ± 1	4 (fixed)	0–7.8				
	108	9	0–35	NaCl, Ag, MgO	NaCl, Ag, MgO	XRD/DP	Ref. 11, 1966
	130	4.13	–	–	–	Calculation/GGA	Ref. 9, 2002
B2	169 ± 7	4.66 (fixed)	102–176	Au	None	ADXRD/DAC	This work, run 2
	114	4.66	–	–	–	Calculation/GGA	Ref. 9, 2002

III. RESULTS AND DISCUSSIONS

Due to the limited pressure range of 9.7 GPa in run No. 1, only the isothermal bulk modulus at zero pressure was estimated by fitting the volume-pressure data according to the second-order Birch-Murnaghan EOS,[18] while the pressure derivative of the bulk modulus B_0 was fixed to be 4. The B_0 value is in good agreement with the experimental results reported by Zhang within their experimental uncertainty. In the experiments of Drickamer *et al.*, various internal pressure markers which also worked as pressure media, such as NaCl, Ag, and MgO, were used at various pressure ranges.[11] These kinds of pressure calibration and pressure medium methods were responsible for the unreasonable values of B_0 and its pressure derivative.

Compared to the experimental data in run No. 1, the B_0 value calculated using the generalized gradient approximation (GGA) was significantly underestimated by about 13.3%.[9] On the other hand, the lattice parameter of CdO was overestimated by about 1.5% as 4.77 Å. In the calculations for ZnO,[10] results from local-density approximation (LDA) and GGA were reported. The GGA corrected the cohesive energy, but overestimated the lattice constant, and also predicted somewhat too small bulk modulus by comparing to the experimental data for its B1 structure.[10] It was pointed that the discrepancy in B_0 may be due in part to the neglect of relativistic effects.[19,20] Even so, the calculations have shown a trend that the structural transition pressure P_{Tc} is underestimated by the LDA but accurately by the GGA for the known B4-to-B1 phase transition in ZnO, as well in similar calculations for other materials.[21,22] These encouraged us to perform further higher-pressure experiments to check the validity of the GGA predicted transition pressure of the B1-to-B2 transition for CdO, because it has potential guiding influences on future high-pressure experiments if the phase transitions could be accurately predicted by this kind of total energy calculations.

The high-pressure experiments of run No. 2 were designed with capability to beyond 100 GPa by using beveled diamonds with culet size of $100~\mu m - 10° - 300~\mu m$. No pressure medium was used in run No. 2 because even helium medium is not hydrostatic above 50–80 GPa pressure

range.[15,23,24] One c-BN backing plate for the diamond anvil was used to obtain full diffraction patterns over a large angular range. A small amount of gold powder was loaded in the sample chamber as pressure marker using the known equation of state of gold.[25] The monochromic beam generated by Si(220) and was focused by a K-B mirror down to about 10 μm in diameter; then, the diffraction patterns of the CdO sample with and without Au could be obtained by selecting the beam position within sample chamber with diameter of 40 μm in run No. 2.

The B_0 and B_0' of the B1 phase were simultaneously fitted by the Birch-Murnaghan EOS, since this set of experimental data within a large pressure range could generate more reliable values of B_0'. The results of $B_0 = 147$ GPa and $B_0' = 4.2$ are consistent with the results in run No. 1 and Zhang's report within the experimental uncertainty, while the GGA calculations deduced $B_0' = 4.13$ and underestimated B_0 as 130 GPa.

Typical high-pressure XRD patterns are displayed in Fig. 1 ($\lambda = 0.4228$ Å) at the pressure range of 84.4–102.5 GPa during the compression process in run No. 2. CdO remained in the B1 structure until it was pressurized to 90.6 GPa, at which pressure new peaks appeared and indexed as B2 structure. The state-of-the-art high-pressure research facilities at HPCAT, APS provide a tunable wavelength which enables one to observe more diffraction peaks via the limited DAC opening by using short wavelengths. Figure 2 demonstrates the diffraction patterns recorded ($\lambda = 0.3678$ Å) under 170 GPa and the corresponding Rietveld refinement result for the B2 structure of CdO (Ref. 26) using the GSAS package.[17] Table I lists the results of the previous reported high-pressure experimental and simulation data for CdO and the results of this work. The impressive correction of the observed P_{Tc} value in the value predicted by the total energy calculations,[9] indeed, proved the astonishing accuracy of the P_{Tc} value obtained by the GGA.

To compare the experimental data with first-principles calculations, run No. 2 was carried out to higher pressure to obtain compressibility data. These data were used to deduce the bulk modulus and cell parameter values of the B2 phase of CdO. The B2 phase remains stable up to the maximum pressure of 176 GPa reached in this run. Figure 3 displays
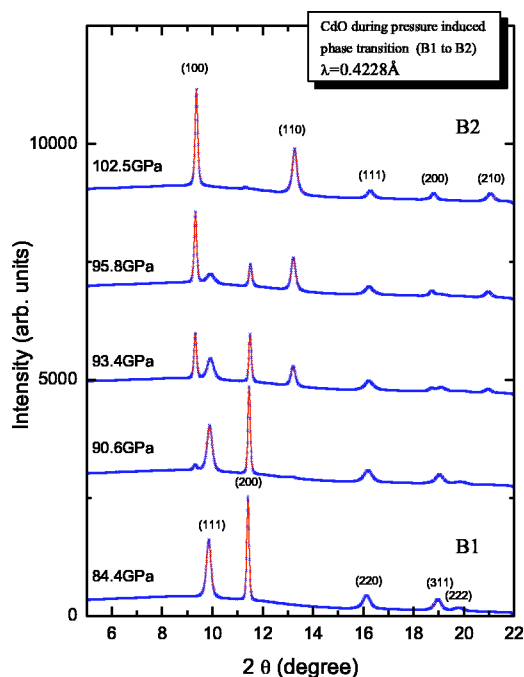
FIG. 1. (Color online) The ADXRD patterns of CdO during the B1-to-B2 phase transition.

the molar volume as a function of pressure. The corresponding B_0 and a_0 of the B2 phase were estimated by fitting the volume-pressure data according to the Birch-Murnaghan EOS while B_0' was fixed at 4.66, which is the same as the B_0' value obtained by simulations[9] of the B2 phase.

The lattice constant of B2 structure at ambient conditions was estimated as about 2.86 Å from ADXRD data, and it was overestimated by about 2.8% as 2.94 Å in the calculations. On the other hand, the calculated values of the bulk modulus are significantly underestimated by about 32.5% for the B2 structure of CdO. It is noticed that the experimental bulk modulus at zero pressure, especially for the high-pressure phase which is stable above 100 GPa, is strongly
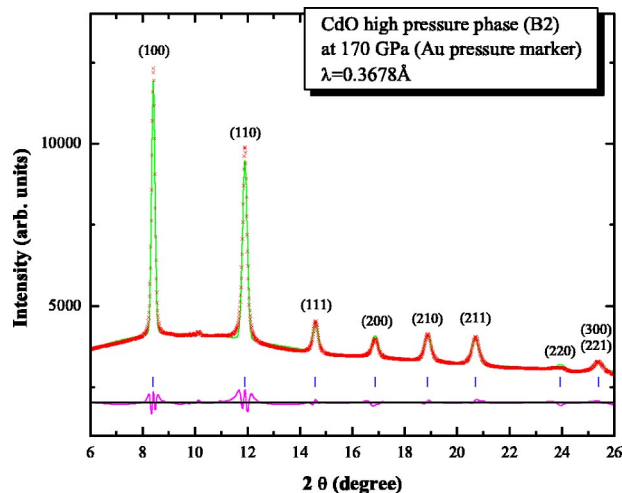

FIG. 2. (Color online) A typical Rietveld refinement result ($R_{wp}=1.66\%$, $R_p=1.23\%$) for the XRD pattern measured under 170 GPa.
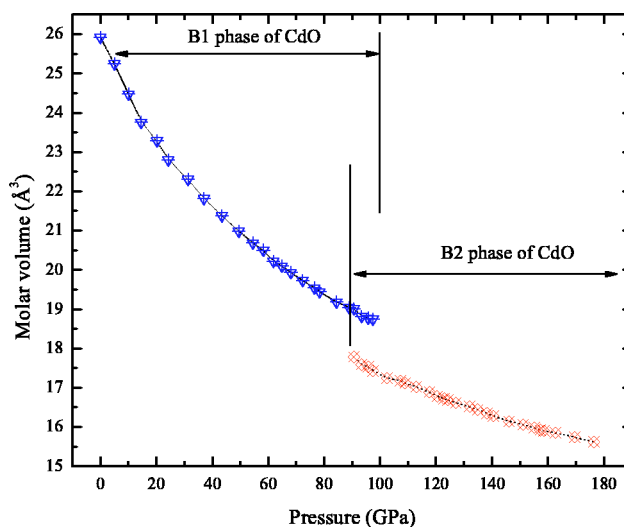

FIG. 3. (Color online) Molar volume of CdO as a function of pressure (the error bars are omitted since they are smaller than the symbol size).

dependent on its pressure derivative when it is fitted. The smaller B_0' value around 3, which somehow reflects the strong compression feature as pressure above 100 GPa, could generate even bigger measured B_0 value.

Although the most previous GGA calculations demonstrated the trend of "softer" crystals (smaller B_0) with larger equilibrium volumes,[8,9,21,22] this still raises the question that, if correct, or at least comparable, lattice constants and the bulk moduli of the B1 and B2 phases of CdO were calculated first, could the correct P_{Tc} be obtained? The theoretical inaccuracies in the calculated lattice constant and bulk modulus values, which arise from the "overcorrect" trend by using of the GGA,[9] are expected to be reduced by using relativistic corrections or by taking into account the screened effective Coulomb interaction parameter U_{eff} in the interaction between localized d electrons[27,28] or utilizing artificially modified basis sets.[29] The improvement in computational work may give more confidence to experimentalists who design an experiment to target a predicted high-pressure transformation based on a similar theoretical frame.

The current high-pressure experimental study responded positively to the total energy calculations on the issue of precisely predicted P_{Tc} in the case of CdO under strong compression. However, the much bigger value of the measured bulk modulus B_0 for B2 phase CdO than its B1 phase attracts attention, because the B_0 value was obviously smaller in the B2 phase than its value in the B1 phase in the calculations.[9] The measured bigger bulk modulus of the B2 phase than the B1 phase CdO could help to evaluate the calculations for the neighborly 3d transition-metal monoxide ZnO. The B1 phase of ZnO was shown to have similar electronic structure character as CdO. These calculations were based on the Hartree-Fock method[30] and density functional theory.[10] By similar total energy calculations for ZnO, a prediction for a B1-to-B2 phase transition pressure will occur at about 256–260 GPa.[10] It is a challenging pressure range to reach for current static high-pressure experimental techniques, so the reliability of the prediction under such high-pressure ex-

treme conditions needs to be critically analyzed.

To simplify this question, assuming the lattice constants were systematically overestimated while the bulk modulus was systematically underestimated for both $B1$ and $B2$ phases in the GGA, and then it has no obvious influences on the predicted phases transition pressure P_{Tc} in ZnO. If ZnO has same trend as CdO in the bulk modulus—i.e., a bigger B_0 value in the $B2$ phase than in the $B1$ phase, instead of its relative lower B_0 value for the $B2$ phase in the calculations for ZnO,[10] this may result in a more bended E-V curve of the potential $B2$ phase to produce a higher bulk modulus. Then the predicted transition pressure, which was estimated based on the overlap between the E-V curves of the $B1$ and $B2$ phases of ZnO, could dramatically increase to an inaccessible pressure range by current static high-pressure experimental techniques, due to the shift towards to small molar volume of the overlap point between these E-V curves. Meanwhile, other possible phases, such as NiAs ($B8$) structure, may become more stable under compression compared to the $B2$ phase. Therefore the calculations for ZnO under high pressure with more candidate structures and in particular bigger B_0 of the $B2$ phase need to perform to clear this prediction of the $B1$-to-$B2$ transition.

Modern computational science has reached a level of accuracy where the theoretical calculations could be used for establishing the "true" behavior of perfect materials, whether materials are realized in nature or not. However, accurate experimental data are still, and will be, the primary standards toward the testing or benchmarking of calculations and simulations. The evaluation for the calculations of transition-metal oxide CdO from this experiment will shed the light on the accuracy of GGA calculations for ZnO. Since the $B1$-to-$B2$ phase transition is associated with several symmetry breaking mechanisms during its consecutive stage,[31] some low-symmetry phase may become more stable in the energy landscape during compression The calculations should take into account the possibility of intermediate pathways and carefully make adjustments for the individual structural case based on the trend of the measured B_0 and a_0 values, if available.

It is noted that the phase transition directly from $B1$ to $B2$ under compression is common in alkali and ammonium halides.[31] This could be explained by the hard sphere model that has a trend from $B1$ structure with coordination number of 6 to $B2$ structure with coordination number of 8 under compression. However, this trend was not observed in the high-pressure research of transition-metal oxides,[2–5] because the characteristic feature of the physics in transition-metal oxides is that the charge, spin, and lattice degrees of freedom are strongly coupled, and these mutual couplings play a crucial role in controlling the phases and various physical properties.[32] In this report, it is found that the $B1$ transforms to $B2$ structure without any intermediate phase as pathway in the transition-metal oxide compounds. Cd is the end member of the transition-metal group; its ground-state electron configuration [Kr] $4d^{10}$ $5s^2$ makes it somehow similar to IIA main group elements since the full filled in its $4d$ orbitals. This may be the reason that its oxide demonstrates different trends in the phase transition sequence from other transition-metal oxides, instead to similar to many IIA-VIA compounds such as CaO, SrO, BaS, etc., as summarized in Ref. 31 for the direct $B1$-$B2$ transition under pressure.

The molar volume change during the $B1$-to-$B2$ phase transition process could also give us the information of the bonding feature. For ionic compounds, the $B1$-to-$B2$ transition takes places on cooling or with increasing pressure always together with large volume change ranging from 10% to 17%, while the more covalently bonded compounds with molar volume change less than 5%, and often take place via low-symmetry intermediate phase.[31] The molar volume change is about 7.3% when the $B1$-to-$B2$ phase transition happened between 90 and 100 GPa, indicating that the CdO somehow steps away from the ideal ionic compound, but does not reach the more covalently bonded range.

IV. CONCLUSION

In summary, *in situ* high-pressure x-ray diffraction experiments were performed up to 176 GPa for CdO, and phase transitions from NaCl- to CsCl-type structure were found around 90 GPa, which is in good agreement with density functional theory total energy calculations. Improvement of the theoretical calculation is expected for the $4d$ and $3d$ transition-metal monoxides CdO and ZnO if these ultrahigh-pressure experimental data of the bulk modulus and lattice constant of the $B2$ phase of CdO could be used as input to the calculations for ZnO.

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