Wurtzite CoO

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Cobalt oxide in the wurtzite modification has been prepared by a nonaqueous solution route and its structure determined using neutron and X-ray powder diffraction. SQUID magnetization measurements and low-temperature neutron diffraction do not show evidence for long range magnetic order, perhaps reflecting magnetic frustration intrinsic to the wurtzite structure type. Density functional calculations of the electronic structure of wurtzite CoO suggest that electron correlations must be explicitly considered in order to correctly describe this unusual material.

Introduction

Transition metal oxides constitute a well-studied class of materials due to their many interesting properties and numerous applications. Cobalt oxide and cobalt oxide-based thin films are useful in a variety of applications such as high-efficiency selective coatings for solar collectors,[1,2] catalysts for electrochemical devices,[3] and solid-state optical gas sensors.[4] Cobalt oxide typically crystallizes in one of two stable phases: rock-salt CoO (space group $Fm\bar{3}m$) with octahedral Co^{2+}, and normal spinel Co_3O_4 ($Fd\bar{3}m$) in which Co^{2+} and Co^{3+} are respectively tetrahedrally and octahedrally coordinated.[5] Both CoO and Co_3O_4 are antiferromagnetic with Néel temperatures of 287 and 40 K, respectively.[5]

Interest in oxides with Co^{2+} in a tetrahedral environment, and particularly in the wurtzite ($P6_3mc$) and/or zinc blende ($F\bar{4}3m$) structures, has been engendered by the suggestion by Dietl and co-workers[6] that wide band gap wurtzite semiconductors such as GaN and ZnO can be rendered ferromagnetic with Curie temperatures on the order of room temperature through substitution of magnetic transition metal ions on the cation sites[7] of these nonmagnetic oxides. We now believe that such substituted zinc oxides would not display ferromagnetism in the absence of significant hole doping.[8−10] It is nevertheless interesting to consider the "end-member" of the wurtzite solid solution $Zn_{1-x}Co_xO$ and, in particular, to determine its structural, magnetic, electronic, and optical properties. Added impetus for making wurtzite CoO arises from the possibility of coupling between structure and magnetism in this potential piezoelectric material. Piezomagnetic coupling has recently been suggested in hypothetical wurtzite MnO.[11]

CoO in the zinc blende structure was first prepared by Redman and Steward[12] by decomposing Co acetate in a nitrogen atmosphere with approximately four percent each of carbon and cobalt metal as impurity phases. More recently,[13] decomposition of cobalt acetate tetrahydrate in argon was studied using time-resolved neutron diffraction and thermogravimetric analysis; in a parallel study, electron microscopy and atomistic simulations were utilized to determine crystal morphologies and predict lattice energies for the rock-salt, zinc blende, and wurtzite polymorphs of CoO.[14] The decomposition was determined to involve loss of water at 150 °C, followed by crystallization of the anhydrous acetate at 200 °C. Subsequent heating led to the formation of either zinc blende CoO at 290 °C or a mixture of zinc blende and wurtzite at 310 °C.

It is important to note that the wurtzite phase has never been formed without the zinc blende phase present,[14] suggesting that the wurtzite polymorph nucleates from zinc blende, perhaps as a stacking fault. At 320 °C, a transformation to rock-salt CoO occurs, in keeping with the preference of Co^{2+} for octahedral coordination. Lattice energy calculations,[13] along with an investigation of the activity−composition relations in the CoO−ZnO system,[16] suggest that when

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the total lattice energies (the sum of the ionic cohesive energy and the octahedral site preference energy) are compared, the rock-salt structure is more stable than the wurtzite structure by 0.27 eV per CoO. Our own studies suggest that working with the acetate is difficult; the material must be heated to precisely 310 °C for less than 1 h in order to obtain zinc blende CoO with a cell parameter of 4.552(1) Å. If the sample is heated for 24 h, a structural transformation to spinel occurs; above 320 °C, the material transforms to rock-salt CoO.

We report here a completely novel approach to nearly pure wurtzite CoO involving the decomposition of cobalt acetylacetonate $Co(CH_3COCHCOCH_3)_2$ in refluxing benzyl ether. Rietveld analysis of neutron and X-ray powder diffraction profiles indicates an unusually distorted wurtzite lattice. Magnetic measurements are dominated by a small ferromagnetic fcc-Co impurity present in the sample and show no evidence of a magnetic transition in wurtzite CoO between 400 and 5 K. This is supported by the 15 K neutron diffraction pattern. Density functional calculations on wurtzite CoO point to the importance of electron correlations in determining the magnetic and electronic ground states of this novel material.

Experimental Section

All chemicals were used as received. One gram (3.9 mmol) of cobalt acetylacetonate [$Co(acac)_2$, Aldrich 97%] was added to approximately 40 g (210 mmol) of benzyl ether (Aldrich 99%) in a three-necked flask equipped with a magnetic stir bar. A water condenser was inserted in the middle neck for refluxing. The two other necks were used to flow nitrogen and for a thermocouple. The solution was heated to reflux with magnetic stirring, between 290 and 293 °C. During heating, the color of the initially pink solution turned purple, and then nearly brownish black. After 1 h, the mixture was cooled, and the solid product was collected by centrifugation and subsequently washed with toluene. The product was dried in air at 80 °C overnight. The powder collected after drying is a deep moss green in color. A closely related preparation starting with $Zn(acac)_2$ resulted in a product mixture comprising nanophase wurtzite and zinc blende ZnO.[15]

X-ray diffraction data were collected on a Scintag X2 diffractometer (Cu Kα radiation, 45 kV, 35 mA) in the Bragg−Brentano reflection geometry using a 0.01° step scan for 6 h between 30 and 90° 2θ.

Neutron data was collected on the Strain Scanner at the Australian Nuclear Science and Technology Organisation's reactor HIFAR. This instrument has a well-shielded, small 32 wire area detector and, with the detector in the close-in position, gives a better signal-to-noise ratio than either of the standard powder instruments at the ANSTO. Data were accumulated for 80 min at each detector position (40 min for the 450 K run). The small sample (70 mg) was contained in an aluminum foil tube 5 mm in diameter and approximately 10 mm long. One end was press-sealed with a fold of cadmium and the other was fitted with a 5 mm diameter aluminum pin which was screwed to the cold head of the cryofurnace. This aluminum pin was masked with cadmium but the foil can (≈20 mg) gave rise to peaks in the diffraction pattern. The temperature given is that of the head to which the aluminum pin was attached.

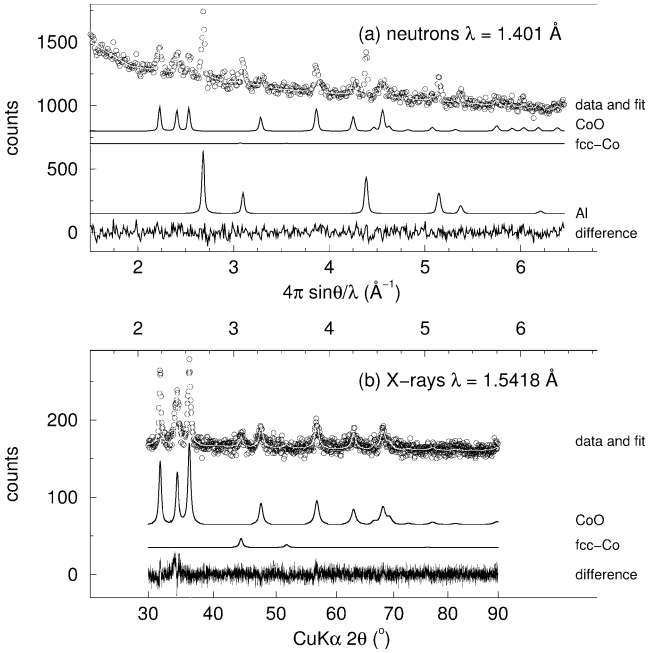

Figure 1. (a) Rietveld refinement of the 300 K powder neutron diffraction pattern of the wurtzite CoO sample. (b) Rietveld refinement of the room-temperature powder X-ray diffraction pattern of the wurtzite CoO sample. The wurtzite structural parameters are as follows: space group $P6_3mc$ (No. 186) $a = 3.244(2)$ Å, $c = 5.203(4)$ Å. Co at ($^1/_3$, $^2/_3$, 0) and O at ($^1/_3$, $^2/_3$, 0.416_2). $R_{Bragg} = 9\%$.

Magnetization measurements as a function of field and temperature were performed on a Quantum Design MPMS 5XL magnetometer between 5 and 400 K, with the powder sample pressed down in a gelatin capsule.

Computational Methods

First principles electronic structure calculations on wurtzite CoO, making use of structural parameters obtained from the Rietveld analysis, were performed using the linear muffin tin orbital (LMTO) method within the atomic sphere approximation[17] as implemented in the Stuttgart TB-LMTO-ASA program.[18] Spin-polarized calculations were performed on a grid of 300 irreducible *k* points in the primitive wedge of the Brillouin zone. The Perdew-Wang[19] formulation of the gradient-corrected exchange correlation potential was employed.

Results and Discussion

Room-temperature powder neutron and X-ray diffraction data for CoO are shown in the two panels of Figure 1. Due to the small sample quantity, along with Co fluorescence in Cu Kα radiation, the neutron and X-ray data are quite noisy. To obtain a reliable structural description of this new material, we have used the XND code[20] to simultaneously refine the structural model against the neutron and X-ray data. At 300 K, there were no peaks in the neutron diffraction pattern corresponding to any magnetic phase. In the refine-

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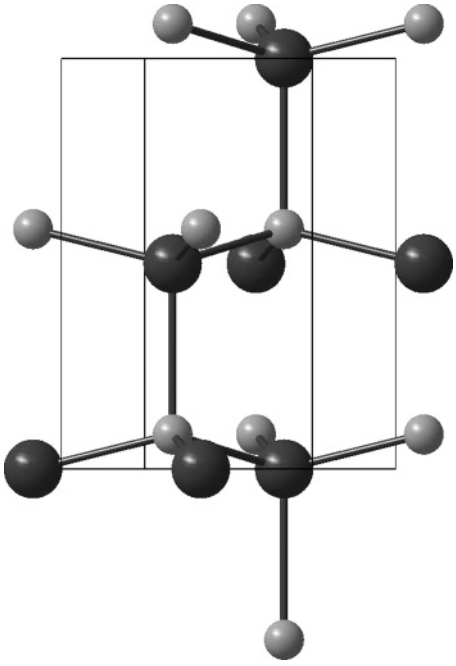

Figure 2. Crystal structure of wurtzite CoO drawn using parameters determined from the Rietveld refinement. Dark spheres are Co and light spheres are O. The large distortion of the wurtzite structure is seen as an elongation of the apical Co−O bond with a Co−O distance of 2.164(1) Å and a bond valence of 0.28. This results in Co residing in a triangle formed by three equatorial O, with a Co−O distance of 1.923(3) Å and a bond valence of 0.54.

ment against the neutron pattern, wurtzite CoO, fcc-Co (determined to be a small impurity in the sample) and the fcc aluminum sample can (with some texturing) were included in the refinement. The X-ray refinement did not include the aluminum can. Co scatters anomalously in Cu Kα X-radiation, and the appropriate f' and f'' terms were included in the refinement. The relative coherent neutron scattering cross sections of Co and O are 5.80 fm and 2.49 fm, respectively. The neutron pattern is therefore dominated by scattering from O, while the X-ray pattern is dominated by scattering from Co. As a consequence of the identical Co and O site symmetries in the wurtzite structure, the neutron and X-ray fits to CoO in both Figures 1a and 1b are rather similar, apart from the usual form-factor decay observed in the X-ray data. The combined refinement, with an $R_{\mathrm{Bragg}} = 9\%$ for the CoO phase, yielded the structural parameters indicated in the caption of Figure 1. The relative amount of the fcc-Co phase [$a = 3.530(5)$ Å] was determined from the Rietveld scale factors to be 12 mol %.

The crystal structure of wurtzite CoO along with bond distances and bond valences are presented in Figure 2 and its caption. We find that wurtzite CoO has an unusually long axial bond distance of 2.164(1) Å, and three shorter "equatorial" distances of 1.923(3) Å with a ratio of 1.13. In contrast, Rietveld refinement of pure ZnO suggests an axial distance of 2.009(5) Å, and equatorial distances of 1.968(1) Å, a ratio of 1.02. The structure is acceptable, with a bond valence sum of 1.9 on Co.

We have so far been unable to prepare wurtzite CoO without the Co metal impurity. It is known that cobalt acetate is easily reduced to cobalt metal in refluxing organic solvents

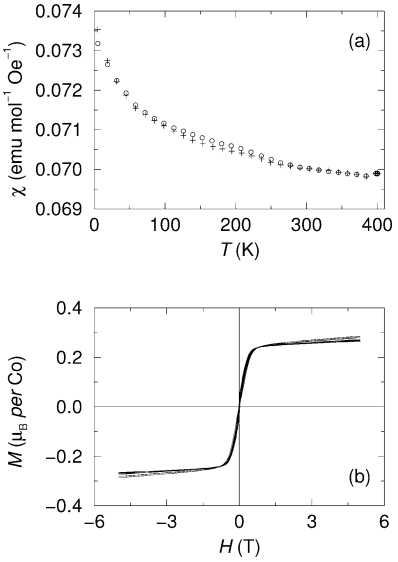

Figure 3. (a) Field-cooled (circles) and zero-field cooled ("+") magnetic susceptibility data for the CoO/Co sample, acquired under a 2 T magnetic field. (b) M vs H of the sample at 7 different temperatures, 5 K, 55 K, ..., 305 K. The magnetization is dominated by the fcc-Co impurity.

in the presence of organic alcohols.[21] While we have not added any extraneous reducing agents, it is possible that the decomposition products of the acetylacetonate serve to create sufficiently reducing conditions that some of the cobalt is reduced. We are currently attempting the use of mild oxidants during the preparation to prevent reduction of $Co(acac)_2$. Due to the very fine-grained nature of the product powder, we have been unable to magnetically separate Co from wurtzite CoO.

Magnetic measurements indicate a ferromagnetic sample, with magnetic susceptibility recorded under a 0.1 T field (not displayed), indicating diverging field-cooled and zero-field-cooled traces as the temperature is lowered. Clearly, the ferromagnetic behavior arises from the second fcc-Co phase and not from wurtzite CoO. In Figure 3a, we show the field-cooled and zero-field-cooled magnetic susceptibility of the sample, recorded under a high (2 T) field in order to saturate the magnetism of the fcc-Co phase. In keeping with the known antiferromagnetic behavior of rock-salt CoO,[22] we would expect that wurtzite CoO is also antiferromagnetic. The absence of any signature of antiferromagnetic ordering in the $\chi-T$ traces is therefore puzzling.

Figure 3b displays magnetization M of the sample as a function of magnetic field, H, acquired at 7 different temperatures: 5 K, 55 K, 105 K...305 K. The magnetization is clearly dominated by the ferromagnetic Co impurity. In keeping with the very high Curie temperature of Co metal (near 1400 K),[23] there is no great change in the magnetization of the ferromagnet in the temperature range measured, and all the $M-H$ traces nearly collapse on to one another. The magnetization is already saturated by about 1 T, justifying our belief that the 2 T susceptibility should be dominated by the behavior of CoO. From the saturation magnetization

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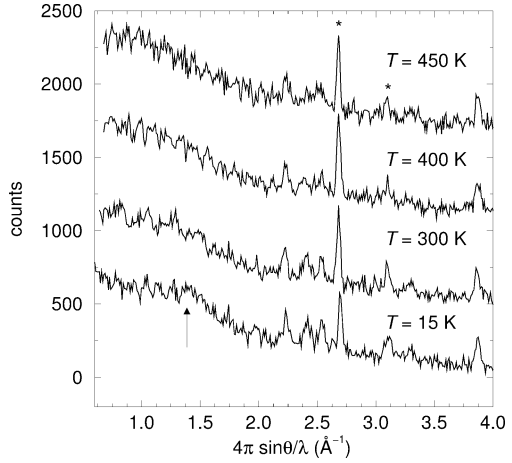

Figure 4. Neutron diffraction patterns of the CoO sample acquired at 450, 400, 300, and 15 K. Asterisks indicate reflections from the Al can. The arrow near the 15 K data indicates a possible hump in the neutron diffraction pattern that could indicate short-range antiferromagnetic ordering.

value of 0.24 μ_B per Co and the listed low-temperature saturation of Co metal of 1.74, we calculate the relative fcc-Co amount to be approximately 14 mol %, in close correspondence with the value obtained from Rietveld refinement.

Since magnetic neutron scattering is phase-specific and unaffected by secondary phases, we have recorded neutron diffraction patterns of the CoO sample at different temperatures down to 15 K, using 1.401 Å neutrons. The patterns are displayed in Figure 4. Even at 15 K, there is no evidence of any new magnetic reflection at low angles, apart from the suggestion of a hump at $4\pi \sin\theta/\lambda = 2\pi/d = 1.3$ Å^{-1}, which is indicated by the arrow. With six unpaired *d* electrons per unit cell, and given the small cell volume, we would expect peaks associated with long range magnetic ordering to be quite strong. The absence of any strong magnetic reflection, the absence of the signature of an antiferromagnetic transition in the $\chi-T$ traces, and the intrinsic frustration of antiferromagnetic interactions on triangular and tetrahedral lattices (exemplified by wurtzite) all add up to a picture of possible magnetic frustration. Frustration and short range order could be the source of the hump in the 15 K neutron pattern at $2\pi/d = 1.3$ Å^{-1}.

An alternate explanation for the absence of well-defined magnetic reflections could be associated with the small particle size of the wurtzite CoO studied here. Scherrer-broadening analysis of the (0002) wurtzite X-ray reflection indicate that the CoO crystals are smaller than 20 nm. Wurtzite-based antiferromagnets such as β-MnS[24] are associated with large magnetic unit cells. The broadening of superstructure reflections would be particularly acute in such small crystallites as the ones observed here and could result in their being indistinguishable from the background. Further experiments on larger sample batches are planned in order to pinpoint the precise nature of magnetic ordering in this novel material.

First principles electronic structure calculations were performed on the experimental crystal structure of CoO for a nonmagnetic cell and a cell with spin polarization (ferromagnetic). The calculations indicate that ferromagnetic spin-polarization stabilizes the CoO unit cell by about 0.4 eV/CoO compared with nonmagnetic CoO.

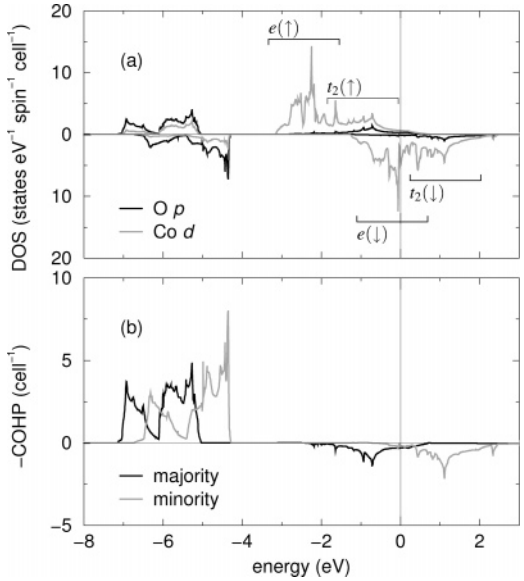

Figure 5. (a) Densities of O p and Co d states in the two spin channels obtained from spin-polarized LMTO calculations on wurtzite CoO using the experimentally determined crystal structure. The origin on the energy axis is the Fermi energy. (b) Crystal orbital overlap populations corresponding to Co−O interactions in the two spin channels (majority and minority).

While the stabilization of a magnetic ground state is unambiguous, we believe that obtaining the correct magnetic ground state would require accounting for electron−electron correlations of the Hubbard-*U* kind which are well-known to be very important in rock-salt CoO. Using a combination of electron spectroscopy and cluster calculations, van Elp et al.[25] have determined that rock-salt CoO has a Hubbard $U = 5.3$ eV and a charge transfer $\Delta = 5.5$ eV.

In Figure 5a the LMTO densities of O p and Co d states in the two spin channels are displayed for spin-polarized CoO. O p states are centered around −6 eV with respect to the Fermi energy, well-separated from Co d states. The separation of p and d states is to be expected for a divalent transition metal compound. Despite such separation, there is significant metal−oxygen covalency as testified by the manner in which O p states are strongly perturbed by the magnetism of Co; this is reflected in the strong exchange splitting of O p states. Evidence for strong covalency is directly obtained from Crystal Orbital Hamiltonian Populations[26] for the Co−O interactions plotted in panel (b) of this figure. COHPs have been calculated separately in the two spin channels; in the absence of spin−orbit coupling, there would be no interaction between majority Co states with minority O states and vice versa. The COHPs reveal that in the region of O p states, there are strong bonding interactions (−COHP > 0) between Co and O in both spin channels. In the region of energy where Co t_2 states are found, the interactions are antibonding (−COHP < 0) in both spin

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channels. In the region where e states are found, there are no interactions with O in accordance with simple crystal field ideas. Spin-polarized LMTO calculations on rock-salt CoO similarly suggest strong exchange splitting of O *p* states, so what is observed here is not uniquely due to the tetrahedral coordination. It is well-established that metal−oxygen covalency plays a significant role in the low-energy physics of oxides of the later transition metals such as cobalt.[25,27]

The electronic configuration of Co^{2+} in a tetrahedral environment can be expected to be high spin, with a small crystal field splitting. In agreement with this picture, the DOS in Figure 5 indicates the following d orbital filling: $e^2(\uparrow)$, $t_2^3(\uparrow)$, $e^2(\downarrow)$, and $t_2^0(\downarrow)$. These crystal field assigments are approximately indicated in Figure 5a. Due to the widths of the different d bands being somewhat large, wurtzite CoO is found within DFT to be a metal, contrary to what one would expect for a green compound. An insulating, antiferromagnetic ground state would be obtained if the bandwidths were narrower than those observed here.[8] The results presented here call for a more complete description of the electronic structure based, for example, on LDA+*U* calculations.[28] It is possible that the introduction of a Hubbard *U* would additionally decrease the extent of the Co−O covalency.

In summary, we have used the thermolytic decomposition of $Co(acac)_2$ in a high-temperature solvent to obtain a nearly pure sample of wurtzite CoO whose crystal structure has been established using neutron and X-ray powder diffraction. An initial attempt at understanding the electronic structure and magnetic properties of wurtzite CoO has been made.

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