Magnetic ordering and magnetodielectric phenomena in CoSeO₄

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Abstract
CoSeO₄ has a structure consisting of edge-sharing chains of Co²⁺ octahedra which are held together by SeO₂⁻ tetrahedra via shared oxygen atoms at the edges of the octahedra. DC magnetization measurements indicate a transition to an ordered state below 30 K. Powder neutron diffraction refinements suggest an ordered state with two unique antiferromagnetic chains within the unit cell. Isothermal magnetization measurements indicate a temperature-dependent field-induced magnetic transition below the ordering temperature. From neutron diffraction, we find that this corresponds to a realignment of spins from the canted configuration towards the c-axis. The dielectric constant shows a change in slope at the magnetic ordering temperature indicating an interplay between the spin and charge degrees of freedom.

((Some figures in this article are in colour only in the electronic version)

1. Introduction

Magnetodielectrics are materials in which the dielectric properties couple to changes in the magnetic order. The ability to find and design new single-phase materials which exhibit this coupling between the spin and charge degrees of freedom has significant technological implications in the development of magnetic sensors and field-tunable dielectrics [1, 2]. Systems showing incommensurate and noncollinear spin structures such as CoCr₂O₄ [3, 4], Mn₃O₄ [5], SeCuO₃ [6], and NiₓV₂O₇ [7] have all been extensively studied to understand the nature of such interactions. Recent work characterizing the magnetoelectric coupling in the magnetic chain compounds MnWO₄ [8], and LiCu₂O₂ [9, 10] indicates that systems with reduced crystallographic dimensionality should be of particular interest because of the strong interplay between the charge, lattice, and magnetic degrees of freedom that occurs in these materials [11, 12]. Reduced dimensionality has also been found to result in nonlinear and canted antiferromagnetic spin structures which break symmetry restrictions and allow electric polarization to develop.

Here we discuss the preparation and detailed magnetic and dielectric characterization of CoSeO₄: a magnetic chain compound which adopts a crystal structure analogous to β-CoSO₄ (figure 1). The orthorhombic unit cell contains chains of octahedrally coordinated Co²⁺ which are bound together by SeO₂⁻ tetrahedra via shared oxygen atoms at the edges of the octahedra. The chains of octahedra are tilted with respect to neighboring chains with the axes of the octahedra tilted by −35° and +35° off the a-axis for the chains on the edge and in the center of the cell respectively. Previous reports have characterized the nuclear and magnetic structure using neutron diffraction [13, 14], but no reports on the magnetic susceptibility or dielectric properties have been made to date, and the effects of magnetic fields have not been fully investigated. Using detailed magnetization, heat capacity, powder neutron diffraction, and dielectric measurements, we show that the transition to long-range antiferromagnetic below 30 K is accompanied by a significant change in the slope of...
of CoNO$_3$ previously reported procedure [16]. Stoichiometric amounts of CoNO$_3$ was added to the solution of Na$_2$CO$_3$ which had H$_2$O with a 2:1 (NaCO$_3$ dark purple precipitate was collected by vacuum filtration and ◦ been preheated to 90 ◦C for several days to produce a light violet powder of anhydrous CoSeO$_4$. Co$_2$CO$_3$OH$_2$ was prepared following a separate previously reported procedure [16]. Stoichiometric amounts of CoNO$_3$·5H$_2$O and Na$_2$CO$_3$ were separately dissolved in H$_2$O with a 2:1 (NaCO$_3$:CoNO$_3$) volume excess. The solution of CoNO$_3$ was added to the solution of Na$_2$CO$_3$ which had been preheated to 90 ◦C. After stirring for 2 h the resulting dark purple precipitate was collected by vacuum filtration and subsequently washed with H$_2$O and ethanol. Purity of the precursors and final product was confirmed by powder x-ray diffraction on a Philips XPERT MPD diffractometer operated at 45 kV and 40 mA.

The temperature dependence of the DC magnetization was measured on well-ground powder samples using a Quantum Design MPMS 5XL SQUID magnetometer. The specific heat data were collected using the semiadiabatic technique as implemented in a Quantum Design physical property measurement system (PPMS), under zero applied field as well as under a 1 T field. The measurement was made by mixing the compound with equal parts by mass of silver powder and pressing into a pellet in order to improve thermal coupling to the stage. The contribution from Ag was measured separately and subtracted. Variable temperature neutron diffraction data under a magnetic field were collected on the BT-1 powder diffractometer at the National Institute of Standards and Technology, Gaithersburg, MD using a wavelength of 2.08 Å. The dielectric properties were measured by attaching polished copper electrodes to opposite faces of a cold-pressed pellet of CoSeO$_4$, using a Quantum Design PPMS for temperature and field control, and an Agilent 4980A LCR meter to measure the capacitance. The identification of any commercial product or trade name does not imply endorsement or recommendation by the National Institute of Standards and Technology.

2. Experimental methods

The title compound was prepared following a previously reported procedure [15] by neutralizing a solution of selenic acid (SeO$_2$ (2.559 g, 23.06 mmol) dissolved in 50 cm$^3$ of water) with Co$_2$CO$_3$(OH)$_2$ (1.629 g, 7.69 mmol) at 70 ◦C and recrystallizing in water. The final crystallization step was performed by allowing the remaining water to evaporate at room temperature over several days. Faceted crystals of dark red CoSeO$_4$·6H$_2$O up to 2 cm on a side were obtained from this procedure. These crystals were ground and dehydrated at 125 ◦C overnight to yield a bright pink powder of CoSeO$_4$·H$_2$O which was subsequently heated at 315 ◦C for several days to produce a light violet powder of anhydrous CoSeO$_4$. Co$_2$CO$_3$(OH)$_2$ was prepared following a separate previously reported procedure [16]. Stoichiometric amounts of CoNO$_3$·5H$_2$O and Na$_2$CO$_3$ were separately dissolved in H$_2$O with a 2:1 (NaCO$_3$:CoNO$_3$) volume excess. The solution of CoNO$_3$ was added to the solution of Na$_2$CO$_3$ which had been preheated to 90 ◦C. After stirring for 2 h the resulting dark purple precipitate was collected by vacuum filtration and subsequently washed with H$_2$O and ethanol. Purity of the precursors and final product was confirmed by powder x-ray diffraction on a Philips XPERT MPD diffractometer operated at 45 kV and 40 mA.

The temperature dependence of the dielectric constant. We also report evidence of a field-induced change in the magnetic structure.

3. Computational methods

Density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) [17, 18] at the experimental lattice parameters. The projector augmented-wave (PAW) method [19] was used together with the local density approximation (LDA) Ceperley–Alder exchange correlation functional [20]. A plane-wave energy cutoff of 500 eV and a 6 × 3 × 9 Γ-centered Monkhorst–Pack [21] k-point mesh corresponding to 162 irreducible k-points were used to sample the Brillouin zone. The tetrahedron method with the Blöchl correction [19] was used for Brillouin zone integrations. Correlation was treated using the LDA + U formalism within the rotationally invariant approach of Liechtenstein et al [22]. The applicability of the LDA + U formalism is validated in the example of d$^9$Co$_2$ because crystal symmetry results in an absence of orbital degeneracy. Several values of U were tested with only qualitative changes to the band structure being found. Therefore a U of 5 eV and a J of 1 eV were chosen to agree with previously published DFT results calculated on octahedrally coordinated Co$^{2+}$ [23].

4. Results and discussion

The high temperature region (200–300 K) of the inverse susceptibility was fitted to the Curie–Weiss equation, C/(T − Θ$_{CW}$). A Curie–Weiss temperature of −36 K and an effective moment $\mu_{eff}$ of 4.38 $\mu_B$ were determined for the data collected under a 1 T field. The effective moment lies between the spin-only value of 3.87 $\mu_B$ and the value of 5.2 $\mu_B$ expected for octahedrally coordinated Co$^{2+}$ ($d^7$, $t^2_2$,$e^3$, $S = 3/2$, $L = 3$) with a fully unquenched orbital contribution as obtained using the relationship $\mu_{L+5} = \sqrt{4S(S+1) + L(L+1)}$ [24]. The existence of an orbital contribution is common from high-spin $d^7$ systems in an octahedral $d^7$ crystal field due to the orbital degeneracy in the $t_2g$ levels. The small reduction of the orbital contribution probably arises from the irregular
Figure 2. Field-cooled (FC, open symbols) and zero-field-cooled (ZFC, closed symbols) magnetic susceptibility of a powder sample of CoSeO₄ acquired under increasing strengths of the external magnetic field. At 30 K, the system orders to an antiferromagnetic state. A weak-ferromagnetic component is found in the 10 mT data, suggested from the separating ZFC and FC traces. Note also that the cusp which indicates the magnetic ordering is smeared out with increasing field strength. Error bars represent ±1σ, which is smaller than the symbols.

octahedral environment of the magnetic sites reducing some hybridization with the surrounding oxygen anions.

Figure 2 shows the temperature dependence of the magnetic susceptibility of CoSeO₄ under a variety of magnetic field strengths. The spins begin to order below 30 K which is very near the expected Curie–Weiss temperature indicating that there is very little frustration from competing exchange interactions. When measured in a 10 mT field, a sudden jump in the susceptibility occurs at 30 K which can be attributed to some weak ferromagnetism which results from a canted antiferromagnetic arrangement of the spins. Measuring the sample in larger fields minimizes the contribution from the weak-ferromagnetic component and gives rise to the cusp-like behavior expected from a well-compensated antiferromagnet. Such behavior has been previously reported for CoSe₂O₅ which has a similar structure consisting of chains of octahedral Co²⁺ [25]. This cusp is found to broaden with increasing field strength indicating that the magnetic order may be driven to a different ground state in the presence of sufficiently large external fields.

To further examine the nature of the field dependence of the magnetic order, isothermal magnetization loops were collected at a variety of temperatures (figure 3). An upturn from the linear field dependence expected for a well-behaved antiferromagnet is found beginning in a field of approximately 2 T at 28 K. The upturn shows a strong temperature dependence, with the field required to induce it increasing to 4.5 T by 18 K and subsequently out of the 5 T range of the magnetometer used here by 10 K. Such a field-induced magnetic transition may be attributed to overcoming of the magnetocrystalline anisotropy of the octahedral Co²⁺ cations which would manifest as a spin-flop transition where the spins realign from one preferred axis to another.

Figure 4(a) shows the specific heat of CoSeO₄ measured in zero field, and under an external magnetic field of 5 T. The specific heat shows a sharp anomaly at the magnetic ordering temperature of 30 K in the absence of an external magnetic field. Application of a 5 T field results in a smearing out of the transition in a manner similar to the behavior observed in the susceptibility data shown in figure 2. The lattice contribution
to the specific heat was approximated by fitting the data above the magnetic transition (50–80 K) to the polynomial expansion $\beta T^3 + \gamma T^5 + \delta T^7$ where $\beta = 3.1e - 4$, $\gamma = -6.8e - 8$, and $\delta = 3.9e - 10$. Such a value for $\beta$ gives a Debye temperature of 334 K.

Subtracting the lattice contribution and integrating $C_p / T$ yields a change in entropy due to magnetic ordering of 2.1 J mol$^{-1}$ K$^{-1}$ and 2.5 J mol$^{-1}$ K$^{-1}$ in zero field and a 5 T field respectively. This value is significantly smaller than the value of 11.5 J mol$^{-1}$ K$^{-1}$ predicted by the Boltzmann equation ($\Delta S = R \ln(2S + 1)$, $S = 3/2$).

This considerable diminution of the spin entropy from what is expected is probably a result of an overestimation of the lattice contribution to the specific heat. This overestimation may be the result of entropy being released above the magnetic ordering transition which can occur in systems with short-range correlations which result from competing magnetic interactions. Such interactions would mean that the temperature range over which we performed the fit actually has a small magnetic contribution present which results in a lattice contribution which is too large. Several attempts to prepare a non-magnetic structural analogue such as ZnSeO$_4$ were made with no success.

To better understand the electronic structure and chemical bonding in the title compound, density functional theory calculations were performed using the LDA $+$ $U$ formalism. Figure 5 illustrates the density of states (DOS) calculated for the experimental room temperature structure of CoSeO$_4$. The DOS shows a significant degree of overlap between the Se p and O p states and between the Co d and O p states below the Fermi energy. However, there is a gap of approximately 250 meV between the Co and Se states. It can be seen that a majority of the Se and O overlap is related to bonding between Se and O3. The O3 position forms two bonds within the Se tetrahedron which are 1.56 Å, short in comparison with the Se–O1 and Se–O2 bond lengths which are 1.74 and 1.78 Å respectively. Such bonding is consistent with the idea that the SeO$_4$ tetrahedron contains two double and two single bonds with surrounding oxygens to satisfy its octet. It is interesting to note that the Se–O3 bonds correspond to the shared oxygens at the corners of the CoO$_6$ octahedra within a single chain. This arrangement of double bonds can be expected to significantly influence magnetic superexchange between the CoO$_6$ chains.

The DOS calculated using the LDA formalism results in metallic densities of state, but by accounting for correlations within LDA $+$ $U$, with $U = 5$ eV and $J = 1$ eV, a gap of approximately 3 eV opens between the occupied and unoccupied minority spins. We also note that the band gap which is approximately 2 eV corresponds to the gap between the highest filled states and unoccupied O p orbitals. The distorted octahedral environment of the Co$^{2+}$ breaks the degeneracy of the unoccupied $d_{z^2}$ and $d_{x^2-y^2}$ as well as the $d_{yz}$ orbitals which lie above the Fermi energy.

The antiferromagnetic state is stabilized by more than 0.5 eV compared to a ferromagnetic alignment of spins. The calculated spin magnetic moment on each Co is 2.72 $\mu_B$ which is slightly reduced from the full value of 3 $\mu_B$ expected for a $d^7$ cation in an octahedral coordination environment. Such a reduction may be associated with the covalent bonding to the surrounding oxygens or may be related to the fact that the calculation is restricted to a collinear spin configuration which is not the true ground state observed via neutron diffraction.

The thermal evolution of the neutron diffraction patterns collected from 300 to 5 K is shown in figure 6 with table 1 showing a summary of refined parameters. The nuclear and magnetic structure of CoSeO$_4$ was refined using the Rietveld method as implemented in the FULLPROF software suite [27]. The peak shape was described using pure Gaussian functions, and the background was fitted by interpolation between regions showing no Bragg reflections. For the magnetic structure, group theoretical analysis was performed using representational analysis as implemented in the program...
Fuess reported the structure in the $Pnma$ standard setting of $k = 7/4$ and $23/4$ of the unit cell as listed in Table 2, with a total magnetic moment.

The spins on each Co align antiferromagnetically down the length of the chain and with respect to the neighboring chains. The spins on each Co occupy a $4a$ Wyckoff site. The Co within the unit cell are: Co1 (0, 0, 0), Co2 (4/3, 0, 1/3), Co3 (0, 0, 0), and Co4 (4/3, 0, 1/3).

Variable temperature neutron diffraction data obtained in zero magnetic field shown in figure 8 agrees well with the previously reported structure of Fuess [14]. We note that while the magnetic structure described by $\Gamma_1$ has spins oriented largely in the $ac$ plane with the moments tilting $60^\circ$ (60$^\circ$) off the $a$-axis, $70^\circ$ (69$^\circ$) off the $b$-axis, and $44^\circ$ (41$^\circ$) off the $c$-axis again at 5 K. The moments within individual chains do not cancel completely with a resulting uncompensated moment along the $a$-axis which is canceled by the neighboring chains. This uncompensated moment within the individual chains may be a source of the weak ferromagnetism observed in small external magnetic fields.

The effect of applying a magnetic field of 7 T is to first reduce the total magnetic moment to $2.6 \mu_B$ at 5 K. The field also causes the spins to reorient with respect to the unit cell. At 20 K the moments form angles of $66^\circ$ off the $a$-axis, $64^\circ$ off the $b$-axis, and $37^\circ$ off the $c$-axis. From examination of the isothermal magnetization measurements in conjunction with the reoriented moments the field-induced magnetic transition appears to correspond to a spin-flop transition onto the $c$-axis.

Figure 9(a) shows the inverse magnetic susceptibility normalized by the fits of the high temperature region (between 200 and 300 K) to the Curie–Weiss formula. Normalizing in this manner emphasizes deviations from the Curie–Weiss equation in the form of short-range correlations between the spins which develop above the ordering temperature [29]. Figure 9(b) shows the temperature dependence of the dielectric constant with a very clear change in slope in the dielectric constant at the magnetic ordering temperature. It should be noted that because the measurements were performed on a cold-pressed pellet of powder, a large degree of void space is present in the sample. Such void space means that the absolute value of the dielectric constant is not necessarily accurate, however, the temperature-dependent behavior was found to be reproducible across different samples.

A similar temperature-dependent behavior has been reported by Nénet et al [30] for a hybrid Cr(III) inorganic–organic material. They find a quadratic change with external magnetic field above the magnetic ordering temperature as well as below and attribute the behavior to the always allowed $P^2H^2$ order parameter.

### Summary

We have discussed the preparation and detailed magnetic and dielectric characterization of a magnetic chain compound. Magnetization and specific heat measurements show a...
transition to a long-range canted antiferromagnetic state below 30 K and a temperature-dependent field-induced magnetic transition. Powder neutron diffraction shows that the spins lie predominantly in the \( ac \)-plane with the moments tilting 60° off the \( a \)-axis, 70° off the \( b \)-axis, and 44° off the \( c \)-axis again at 5 K. Temperature-dependent measurements of the dielectric constant show an anomaly at the magnetic ordering temperature. Such behavior indicates that the changes in the dielectric constant result from some interplay between the spins and the charge degrees of freedom.

Figure 8. Proposed magnetic structure of CoSeO₄ as determined from Rietveld refinements of the neutron diffraction pattern obtained using \( \lambda = 2.08 \) Å at 2 K. (a) View down the \( b \)-axis of the \( Pnma \) structure. (b) View down the \( c \)-axis. The small light gray atoms are oxygen while the larger and darker gray atoms are selenium.

Figure 9. (a) Inverse magnetic susceptibility normalized by the values extracted from fits to the Curie–Weiss formula in the high temperature region. Note that this manner of plotting emphasizes short-range correlations which cause deviations from ideal Curie–Weiss behavior which is illustrated as the dashed line. (b) Temperature dependence of the dielectric constant of CoSeO₄ measured on a pressed pellet of a polycrystalline sample at a frequency of 1 MHz. Recall that the absolute value of the dielectric constant is not meaningful because of the significant amount of void space in the sample. The vertical dashed line is a guide to emphasize the transition at the magnetic ordering temperature. Error bars represent ±1σ, which is smaller than the symbols.

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References

[1] Lawes G, Kimura T, Varma C M, Subramanian M A, Rogado N, Cava R J and Ramirez A P 2009 Magnetodielectric effects at magnetic ordering transitions Prog. Solid State Chem. 37 40–54
[2] Hur N, Park S, Sharma P A, Guha S and Cheong S-W 2004 Colossal magnetodielectric effects in DyMn₂O₅ Phys. Rev. Lett. 93 107207
[3] Yamasaki Y, Miyasaka S, Kaneko Y, He J-P, Arima T and Tokura Y 2006 Magnetic reversal of the ferroelectric polarization in a multiferroic spinel oxide Phys. Rev. Lett. 96 207204
[4] Lawes G, Melot B, Page K, Ederer C, Hayward M A, Proffen Th and Seshadri R 2006 Dielectric anomalies and spiral magnetic order in CoCr₂O₄ Phys. Rev. B 74 024409
[5] Tackett R, Lawes G, Melot B C, Grossman M, Toberer E S and Seshadri R 2007 Magnetodielectric coupling in MnO₂ Phys. Rev. B 76 024409
[6] Lawes G, Ramirez A P, Varma C M and Subramanian M A 2003 Magnetodielectric effects from spin fluctuations in isostructural ferromagnetic and antiferromagnetic systems Phys. Rev. Lett. 91 257208
[7] Lawes G et al 2005 Magnetically driven ferroelectric order in Ni₂V₂O₇ Phys. Rev. Lett. 95 087205
[8] Taniguchi K, Abe N, Takenobu T, Iwasa Y and Arima T 2006 Ferroelectric polarization flop in a frustrated magnet MnWO₄ induced by a magnetic field Phys. Rev. Lett. 97 097203
[9] Masuda T, Zheludev A, Roessli B, Bush A, Markina M and Vasiliev A 2005 Spin waves and magnetic interactions in LiCu₂O₂ Phys. Rev. B 76 024405
[10] Park S, Choi Y J, Zhang C L and Cheong S-W 2007 Ferroelectricity in an \( S = 1/2 \) chain cuprate Phys. Rev. Lett. 98 057601
[11] Cheong S-W and Mostovoy M 2007 Multiferroics: a magnetic twist for ferroelectricity Nat. Mater. 6 13–20
[12] Kimura T 2007 Spiral magnets as magnetoelectrics Annu. Rev. Mater. Res. 37 387–413
[13] Fuess H and Will G 1968 Bestimmung der kristallstruktur der selenate MSeO₄ (M = Mn, Co, Ni) durch roentgen- und neutronenbeugung Z. Anorg. Allg. Chem. 358 125–37
[14] Fuess H 1969 Magnetic structures of NiSeO₄ and CoSeO₄ and determination of Néel points of MnSeO₄, CoSeO₄ and NiSeO₄ Z. Angew. Phys. 27 311
[15] Koleva V and Stoilova D 1997 Thermal dehydration of cobalt selenate hydrates Thermochim. Acta 296 31–6
[16] Uzunova E, Klissurski D, Mitov I and Stefanov P 1993 Cobalt-iron hydroxide carbonates as a precursor for the synthesis of high-dispersionity spinel mixed oxides Chem. Mater. 5 576–82
[17] Kresse G and Furthmüller J 1996 Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set Phys. Rev. B 54 11169–86
[18] Kresse G and Joubert D 1999 From ultrasoft pseudopotentials to the projector augmented-wave method Phys. Rev. B 59 1758–75
[19] Blöchl P E, Jepsen O and Andersen O K 1994 Improved tetrahedron method for Brillouin-zone integrations Phys. Rev. B 49 16223
[20] Ceperley D M and Alder B J 1980 Ground state of the electron gas by a stochastic method Phys. Rev. Lett. 45 566–9
[21] Monkhorst H J and Pack J D 1976 Special points for Brillouin-zone integrations Phys. Rev. B 13 5188–92
[22] Liechtenstein A I, Anisimov V I and Zaanan J 1995 Density-functional theory and strong interactions: orbital ordering in Mott–Hubbard insulators Phys. Rev. B 52 R3467–70
[23] Ederer C and Spaldin N A 2006 Origin of ferroelectricity in the multiferroic barium fluorides BaMF₄: a first principles study Phys. Rev. B 74 024102
[24] Day M C and Selbin J 1960 Theoretical Inorganic Chemistry 2nd edn (New York: Reinhold Book Corporation)
[25] Melot B C, Paden B, Seshadri R, Suard E, Névert G, Dixit A and Lawes G 2010 Magnetic structure and susceptibility of CoSe₂O₃: an antiferromagnetic chain compound Phys. Rev. B 82 014411
[26] Žák Z 1980 Crystal structure of diselenium pentoxide Se₂O₅ Z. Anorg. Allg. Chem. 460 81–5
[27] Rodríguez-Carvajal J 1993 Recent advances in magnetic structure determination by neutron powder diffraction Physica B 192 55–69
[28] Wills A S 2000 A new protocol for the determination of magnetic structures using simulated annealing and representational analysis (SARAh) Physica B 276 680
[29] Melot B C, Drewes J E, Seshadri R, Stoudenmire E M and Ramirez A P 2009 Magnetic phase evolution in the spinel compounds Zn₁₋ₓCoxCr₂O₄ J. Phys.: Condens. Matter 21 216007
[30] Névert G, Adem U, Bauer E M, Bellitto C, Righini G and Palstra T T M 2008 Magnetodielectric coupling of a polar organic–inorganic hybrid Cr(II) phosphonate Phys. Rev. B 78 054443