

Articles

Contribution from the Department of Chemistry,
Brown University, Providence, Rhode Island 02912

Dependence of Magnetic Properties on Structure in the Systems NiMoO₄ and CoMoO₄

K. SIEBER, R. KERSHAW, K. DWIGHT, and A. WOLD*

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The defect rock-salt phases of NiMoO₄ and CoMoO₄ were prepared, and their magnetic susceptibilities were measured. The μ_{eff} values for nickel and cobalt were consistent with Ni(II) (3d⁸) and high-spin Co(II) (3d⁷), and the Θ values were 20 and 12 K, respectively. When NiMoO₄ or CoMoO₄ was pressed at 50 kbar, the resulting product crystallized with the wolframite structure. The Θ values for the high-pressure phases of nickel and cobalt molybdate were -102 and -105 K, respectively. The difference in the magnetic properties between the high- and low-pressure polymorphs was found to be consistent with the results of an analysis of the magnetic interaction paths in the defect rock-salt structure relative to the wolframite structure.

Introduction

Tellefsen¹ has studied the change in magnetic properties introduced by the high-pressure transformation of olivine to spinel in the system FeSi_{1-x}Ge_xO₄. These structure types are of geological interest,^{2,3} and it was found that the more negative Weiss constant (Θ) of the olivine compared with that of the high-pressure spinel polymorph could be related to the relative strengths of antiferromagnetic nearest-neighbor interactions present in both structures. Another structure type of geological interest is wolframite⁴⁻⁷ (Fe_{1-x}Mn_xWO₄), and it is found as one of the polymorphs of the divalent transition-metal molybdates.⁸⁻¹⁰

Both nickel and cobalt molybdate crystallize at ambient temperature and pressure with a defect rock-salt structure^{11,12} and will transform with pressure to the wolframite structure.^{8,10} Magnetic measurements of the defect rock-salt phases show the materials to be antiferromagnetic, having low Néel temperatures (T_N) and small values for the Weiss constant (Θ).¹³ Less is known about the magnetic properties of the wolframite phases. In this study, the magnetic properties of NiMoO₄ and CoMoO₄ were determined before and after high-pressure phase transformation and correlated with the nature of cation distribution in the two structures.

Experimental Section

Sample Preparation. Polycrystalline NiMoO₄ was prepared by the solid-state reaction of NiO (obtained by the thermal decomposition of nickel oxalate precipitated from a nickel(II) sulfate solution) and MoO₃ (Johnson Matthey "Specpure" 99.99%). Mixtures of the reactants weighing ~1 g were heated in silica boats in air at 700 °C for 48 h with intermittent grindings. Single-phase products were indicated by X-ray diffraction.

CoMoO₄ was prepared from stoichiometric mixtures of the binary oxides by chemical vapor transport using tellurium(IV) tetrachloride

as a transport agent. CoO was obtained by the thermal decomposition of cobalt nitrate (Mallinckrodt, analytical reagent), followed by heating the resulting oxides in a silica boat for 24 h at 1100 °C under nitrogen. Reaction mixtures of approximately 0.5 g were placed in silica tubes (12 mm i.d. × 15 cm), and a concentration of 2.3 mg TeCl₄ was used; the temperature of the charge zone was 880 °C and that of the growth zone 800 °C. Transport proceeded for 6 days. Upon cooling, the products were removed from the tube, washed immediately with dilute hydrochloric acid, and then rinsed with water and dried with acetone.

High-pressure synthesis was performed with the use of a belted anvil press described by Hall.¹⁴ Samples were ground thoroughly, moistened with 30% hydrogen peroxide to retard reduction of molybdenum(VI) to molybdenum(IV), and squeezed in Teflon holders with the application of full pressure before heating. At the end of a run, sample heating was stopped 15 min before the pressure was released. Pyrex sample holders were used when temperatures exceeded 500 °C.

Sample Characterization. Powder diffraction patterns were obtained with the use of a Norelco diffractometer, employing monochromatic high-intensity Cu K α_1 radiation ($\lambda = 1.5405 \text{ \AA}$). Fast scans at 1° (2 θ)/min were examined for the presence of impurity phases. Lattice parameters were determined by a least-squares analysis of slow scans at 0.25° (2 θ)/min in the range of 10°-70° (2 θ).

Magnetic susceptibility measurements were performed from 77 to 300 K by using a Faraday balance described elsewhere.¹⁵ Field-dependent measurements were made with magnetic field strengths between 6.2 and 10.4 kOe, and the balance was calibrated with platinum wire ($\chi_g = 0.991 \times 10^{-6} \text{ emu/g}$ at 275 K).

Results and Discussion

Both the defect rock-salt structure¹¹ and the wolframite structure¹⁶⁻¹⁸ have all cations in octahedral coordination. The structures can be described in terms of the various linkages of octahedra. The defect rock-salt structure consists of M₄O₁₆ blocks that are made up of four edge-sharing octahedra of the same cation. The M₄O₁₆ blocks are arranged in alternating layers of blocks of the same cation. Within a layer, the M₄O₁₆ blocks are isolated from each other and share corners and edges with the M₄O₁₆ of different cations in the layers above and below, thus producing infinite chains of alternating M₄O₁₆ blocks along the crystallographic *c* axis. The defect rock-salt structure is shown in Figure 1.

In the wolframite structure, octahedra containing the same cation share skew edges, producing infinite zigzag chains ex-

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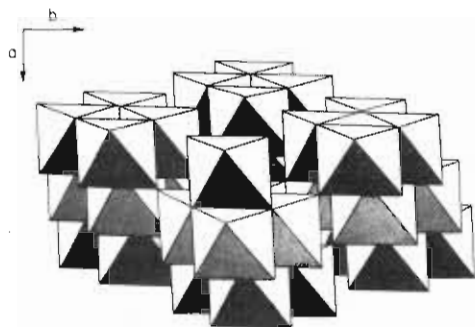


Figure 1. Defect rock-salt structure showing packing of $[\text{MO}_6]$ octahedra in M_4O_{16} units. Unshaded octahedra are $[\text{MoO}_6]$.

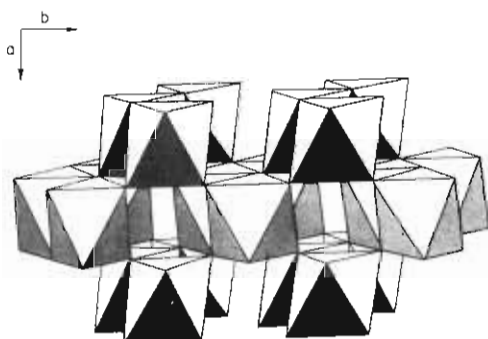


Figure 2. Wolframite structure showing packing of $[\text{MO}_6]$ octahedra along the c direction. Unshaded octahedra are $[\text{WO}_6]$.

Table I. Crystallographic Parameters

	$a, \text{\AA}$	$b, \text{\AA}$	$c, \text{\AA}$	β
NiMoO_4 (DR) ^a	9.491 (1)	8.686 (1)	7.646 (1)	114.12 (5)
CoMoO_4 (DR)	9.708 (1)	8.863 (1)	7.639 (1)	114.01 (5)
FeMoO_4 (DR)	9.794 (1)	8.955 (1)	7.652 (1)	114.04 (5)
NiMoO_4 (W) ^b	4.592 (1)	5.684 (1)	4.879 (1)	90.55 (5)
CoMoO_4 (W)	4.652 (1)	5.677 (1)	4.913 (1)	90.41 (5)

^a DR: defect rock salt. ^b W: wolframite.

tending along the c axis. The chains are arranged in alternating layers of chains of the same cation. Within a layer, separate chains are isolated and share corners with the octahedra in the chains of different cations in the layers above and below. The wolframite structure is shown in Figure 2.

For antiferromagnetic compounds crystallizing with the defect rock-salt or wolframite structures, the Weiss constant (θ) may be considered a measure of the strength of antiferromagnetic interactions. Where paramagnetic ions are isolated, these interactions might be expected to be small. Where they are not isolated, more extensive interactions may be possible.

Defect Rock-Salt Phases. NiMoO_4 is light green, and ground powders of CoMoO_4 are olive green. The compounds crystallize with the defect rock-salt structure (space group $C2/m$) at ambient temperature and pressure. The observed cell constants listed in Table I agree with values in the literature.^{8,12} The magnetic susceptibility data for these materials obey the Curie-Weiss law in the region 100–300 K. The parameters listed in Table II were determined by the method of least squares. The μ_{eff} values for CoMoO_4 and NiMoO_4 (5.39 and 3.24 μ_{B} , respectively) are slightly higher than the theoretical spin-only moments for Co(II) and Ni(II) but agree with μ_{eff} values reported in the literature¹³ and are consistent with the range of μ_{eff} found for these ions in other magnetic studies.^{13,19} The Weiss constants for these compounds with

Table II. Magnetic Properties

	$\mu_{\text{eff}}, \mu_{\text{B}}$	$\mu_{\text{theo}}, \mu_{\text{B}}$	θ, K
NiMoO_4 (DR) ^a	3.24	2.83	20
NiMoO_4 (W) ^b	3.34	2.83	-102
CoMoO_4 (DR)	5.39	3.87	12
CoMoO_4 (W)	5.34	3.87	-105
FeMoO_4 (DR)	5.08	4.90	26

^a DR: defect rock salt. ^b W: wolframite.

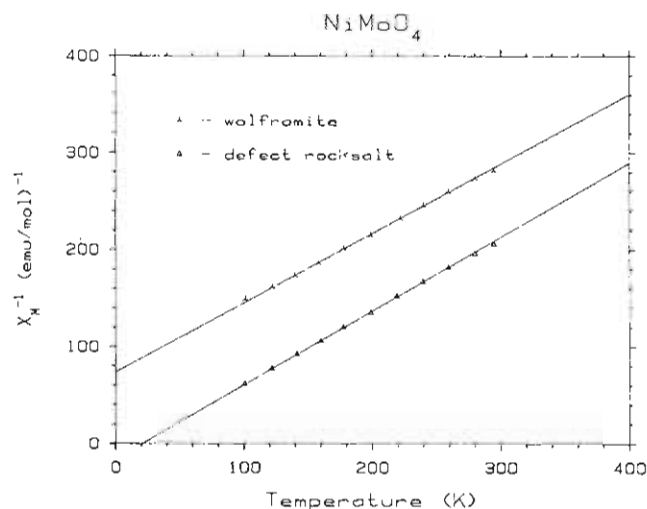


Figure 3. Temperature dependency of the molar magnetic susceptibility of the high- and low-pressure forms of NiMoO_4 .

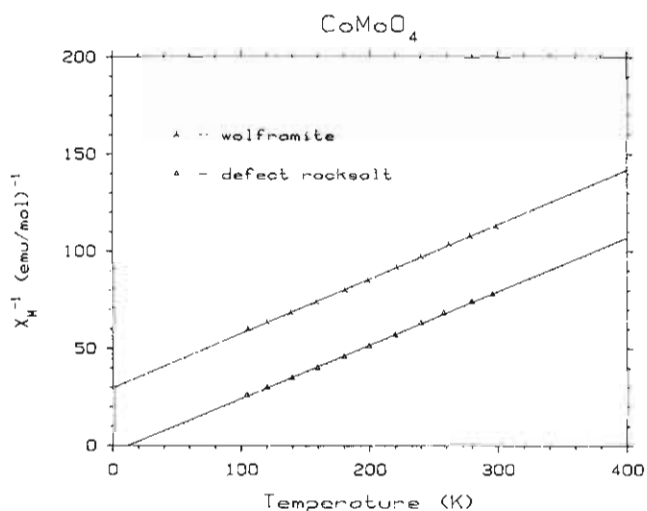


Figure 4. Temperature dependence of the molar magnetic susceptibility of the high- and low-pressure forms of CoMoO_4 .

the rock-salt structure are all small and positive. This indicates that the antiferromagnetic interactions are relatively weak in these materials and are consistent with the low Néel temperatures reported.

High Pressure. Young and Schwartz¹⁰ reported the formation of a wolframite phase of NiMoO_4 and CoMoO_4 at 60 kbar and 900 °C. Sleight⁸ has since reported the preparation of wolframite phases of NiMoO_4 and CoMoO_4 at 65 kbar and 900 °C and at 700 °C and 3 kbar hydrothermally. In this study, it was found that the attempted transformation of NiMoO_4 powder at 50 kbar and 900 °C resulted in the formation of MoO_2 in addition to the wolframite phase, as indicated by X-ray diffraction. Transformation of NiMoO_4 to the pure wolframite phase was achieved by squeezing at 50 kbar and 400 °C in the presence of 30% hydrogen peroxide for 60 min; transformation of single-phase CoMoO_4 was achieved at 350 °C under the same conditions. The resulting wolframite phases of NiMoO_4 and CoMoO_4 are orange and

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light brown, respectively. The cell constants of the high-pressure wolframite phase (space group $P2_1/c$) listed in Table I are in agreement with literature values.^{8,10,20}

The Curie-Weiss plots for NiMoO_4 and CoMoO_4 before and after squeezing are given in Figures 3 and 4. The high-pressure phases show Curie-Weiss behavior in the temperature region between 100 and 300 K. The magnetic parameters are listed in Table II; a comparison of the Weiss constant before and after squeezing indicates that the antiferromagnetic interactions are stronger in the wolframite structure compared to the defect rock-salt structure. This same behavior has been reported in the high- and low-pressure polymorphs of FeMoO_4 , where the values of the Weiss constant are given as -105 and +40 K, respectively.⁹

The existence, nature, and onset temperature of magnetic ordering depend in detail upon the topology of the exchange interactions present in the material.²¹ The Weiss constant Θ , however, depends only on the average value of the arithmetic sum of all the magnetic-exchange interactions in which each ion participates. Thus, the dependence of Θ upon structure can readily be elucidated by the technique of path analysis.²² Both high-spin cobalt $3d^7$ and nickel $3d^8$ possess half-filled e_g orbitals. Consequently, by the Goodenough-Kanamori rules, their $\{\sigma\sigma\}$ magnetic superexchange interactions will be strongly antiferromagnetic.²³⁻²⁵ The t_{2g} orbitals are filled in nickel and more than three-quarters filled in cobalt. Hence, by the rules of superexchange, their $\{\sigma\pi\}$ and weaker $\{\pi\pi\}$ interactions will be ferromagnetic. In both the defect rock-salt and wolframite structures, the nearest-neighbor orbital overlaps are of the $\{\sigma\pi\}$ configuration and yield ferromagnetic interactions for cobalt and nickel. From the straightforward enumeration of interaction paths, it can be seen that each 3d ion has exactly 2 nearest neighbors in the

wolframite structure but averages 2.5 in the defect rock salt. Similarly, each 3d ion participates in an average of 5 antiferromagnetic more-distant-neighbor $\{\sigma\Delta\sigma\}$ and 10.5 ferromagnetic $\{\sigma\Delta\pi\}$ interactions in the defect rock salt, compared with 20 antiferromagnetic more-distant-neighbor $\{\sigma'\Delta\sigma'\}$ interactions in the wolframite structure. (Here Δ denotes the anion-anion overlap of Mo ligands and σ' denotes a $135^\circ e_g$ -anion bond.) This simplified path analysis suffices to show that the Weiss constant Θ should be more positive (ferromagnetic) for CoMoO_4 and NiMoO_4 with the defect rock-salt structure than with the wolframite, in agreement with experiment.

Conclusions

The divalent transition-metal molybdates of cobalt and nickel were prepared, and their magnetic susceptibilities were measured. The μ_{eff} values for the ambient temperature and pressure defect rock-salt phases of cobalt and nickel molybdate were consistent with high-spin Co(II) and Ni(II), and the small positive Θ values of 12 and 20 K, respectively, indicate that the antiferromagnetic interactions in the defect rock-salt structures are balanced by ferromagnetic interactions.

When the defect rock-salt phases of NiMoO_4 and CoMoO_4 were pressed at 50 kbar and 400 and 350 °C, respectively, the resulting product crystallized with the wolframite structure. The Θ values for the high-pressure phases were -102 K for NiMoO_4 and -105 K for CoMoO_4 . The difference in the Θ values before and after pressing indicates a strengthening of antiferromagnetic interactions in the wolframite structure compared to the defect rock-salt structure. This is consistent with the results of a path analysis of the superexchange linkages present in the defect rock-salt and wolframite structures.

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Registry No. NiMoO_4 , 14177-55-0; CoMoO_4 , 13762-14-6; TeCl_4 , 10026-07-0; FeMoO_4 , 13718-70-2.

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Contribution from Ames Laboratory—DOE¹ and the Department of Chemistry, Iowa State University, Ames, Iowa 50011

Core Photoelectron Shifts in Reduced Zirconium Halides. Relaxation Effects and Delocalized Metal-Metal Bonding

JOHN D. CORBETT

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Trends in binding energies of the zirconium $3d_{5/2}$ and chlorine $2p_{3/2}$ levels for Zr , ZrCl_n ($n = 1-4$), ZrBr , ZrXH_x ($X = \text{Cl}, \text{Br}; x = 0.5, 1$), and $\text{ZrClO}_{0.4}$ are considered as a function of oxidation state. The zirconium binding energy exhibits a regular and consistent increase on oxidation for all phases with formal oxidation states between 0 and +2, while those for ZrCl_3 and ZrCl_4 are displaced about 1.3 eV to higher binding energy. Structural and property data for the compounds suggest that the break in zirconium binding energy takes place at the point at which metal-metal bonding and the consequent valence-electron delocalization cease. This effect is considered in terms of the metal valence bands and the final-state relaxation processes that occur in response to the core hole. The apparent relaxation is otherwise remarkably insensitive to differences in valence bands and structure. The only change of significance seen in the chlorine data reflects the different Fermi level reference in ZrCl_4 .

Introduction

The energies of core photoelectron emission events are well-known for their direct reflection of changes in valence-electron distributions that come about either through formal oxidation or reduction or by simple inductive (polarization) effects.²⁻⁴ Although the changes are usually qualitatively

predictable, the origins of the observed binding energies are quite complex. Part of this derives from the fact that the

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