Thermophysical measurements on transition-metal tungstates
II. Heat capacities of antiferromagnetic nickel and cobalt tungstates

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The heat capacity of nickel tungstate (NiWO₄) was measured over the temperature range 5 to 350 K by adiabatic calorimetry, and that of cobalt tungstate (CoWO₄) from 5 to 550 K. Temperatures of maximum heat capacities for the antiferromagnetic anomalies in cobalt and nickel tungstates were (47.6 ± 0.1) K and (59.8 ± 0.05) K. Excess entropies associated with the antiferromagnetic anomalies were evaluated as $R \ln 2$ (1.38 cal K⁻¹ mol⁻¹) for CoWO₄ and $R \ln 3$ (2.18 cal K⁻¹ mol⁻¹) for NiWO₄ with the lattice heat capacities of the compounds approximated by that of ZnWO₄. In addition, the heat capacity of CoWO₄ showed a continuing excess heat capacity consistent with a Schottky anomaly from energy levels lying roughly 600 to 3400 cal K⁻¹ mol⁻¹ above the ground state. Selected thermal functions: $C_p$, $S$°, and $-\langle (G(T) - H°(0))/T$ at 298.15 K are respectively 28.41, 30.08, and 14.01 cal K⁻¹ mol⁻¹ for CoWO₄ and 27.77, 28.51, and 13.21 cal K⁻¹ mol⁻¹ for NiWO₄.

Introduction

The first-row transition-element metal tungstates: MnWO₄, FeWO₄, CoWO₄, NiWO₄, and ZnWO₄, form an isostructural series of compounds in which the number of 3d electrons increases from 5 in MnWO₄ to 10 in ZnWO₄. The crystal structure of these compounds is of the NiWO₄-type,¹ space group P2₁/c (C₁₂₁) and the lattice parameters increase gradually (but irregularly) along the series.² Because the 3d shell is incomplete, MnWO₄, FeWO₄, CoWO₄, and NiWO₄ are paramagnetic at 300 K. At low temperatures, the compounds undergo cooperative transitions to antiferromagnetically-ordered states as shown by both magnetic susceptibility measurements³⁻⁵ and magnetic structures determined by neutron diffraction.⁶⁻⁸ FeWO₄, CoWO₄, and NiWO₄ share a common magnetic structure in which the moments lie in the $ac$-plane, inclined to the $a$-axis by angles of 29° for FeWO₄,⁷ between 20 and 45° for CoWO₄,⁸⁻¹⁰ and 15° for NiWO₄¹¹ The magnetic cell is double the crystallographic unit cell along the $a$-axis with the two moments in each

¹ The previous paper in the series is reference 14.
² This work has been supported by the National Science Foundation, contracts NSF GP-33424X and NSF GP-42525X.
³ To whom correspondence concerning this paper should be addressed.
cell parallel to one another and antiparallel to the pairs adjacent to them along the a-axis. This arrangement implies ferromagnetic layers within the chains in each bc-plane, coupled antiferromagnetically to the adjacent planes (compare figure 1). The magnetic space group (Shubnikov group) for this structure is P2_1/c. The more complicated magnetic structure of MnWO₄ is discussed by Dachs.³⁵

![Figure 1. Magnetic structure of iron (II), nickel, and cobalt tungstates, after Ülkü.](image1)

Measurement of the heat capacities of magnetic compounds yields valuable information concerning the magnetic disordering process as well as the magnetic entropy. The observed heat capacity is a combination of the magnetic disordering, of lattice vibrations, and—sometimes—of the population of nearby excited electronic states. To estimate the lattice contribution to the total heat capacity, the heat capacity of the isomorphous diamagnetic compound, ZnWO₄, is used.³⁵,³⁶

**Experimental**

**SAMPLE PREPARATION AND CHARACTERIZATION**

**Cobalt tungstate.** The sample of cobalt tungstate purchased from Alfa Inorganics who had obtained it from Sylvania, Inc., waslabelled “Crystal Grade”, and had a stated purity of 99.96 moles per cent. The material was amorphous and showed no diffraction lines in preliminary X-rays analyses, but after firing in air at 1120 K for 20 h in a platinum crucible yielded a sharp X-ray pattern which revealed the presence of WO₃ impurity lines in addition to the CoWO₄ lines. Since WO₃ is soluble in alkali, the CoWO₄ was rinsed in 1 M KOH(aq), distilled water, then in 1 M HCl(aq) and again in water.† After drying in a drying oven, the sample was pressed to a pellet with 120 MPa pressure and fired for 30 h at 1275 K.

Since X-ray-diffraction analysis showed faint traces of WO₃ still present in the sample, the CoWO₄ was leached in 50 cm³ batches in 400 cm³ of 1 M KOH(aq) for 15 min. Each batch was then filtered, rinsed in distilled water, rinsed in 0.2 M HCl(aq) (to remove traces of alkali), and finally rinsed in distilled water. The sample was pelleted and fired as before. Subsequent X-ray-diffraction analyses showed no impurity lines and the lattice parameters derived for the CoWO₄ are in good accord.

† Throughout this paper M = mol dm⁻³; cal, = 4.184 J; Torr = (101.325/760) kPa.
HEAT CAPACITIES OF NICKEL AND COBALT TUNGSTATES

TABLE 1. Derived lattice parameters of cobalt tungstate

<table>
<thead>
<tr>
<th>a/nm</th>
<th>b/nm</th>
<th>c/nm</th>
<th>β</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.467 ± 0.001</td>
<td>0.569 ± 0.001</td>
<td>0.494 ± 0.001</td>
<td>90°</td>
<td>Brochu (16)</td>
</tr>
<tr>
<td>0.4669 ± 0.0003</td>
<td>0.5683 ± 0.0003</td>
<td>0.4948 ± 0.0003</td>
<td>90°</td>
<td>Swanson et al. (16)</td>
</tr>
<tr>
<td>0.4667 ± 0.0001</td>
<td>0.5681 ± 0.0001</td>
<td>0.4947 ± 0.0001</td>
<td>90°</td>
<td>Sleight (23)</td>
</tr>
<tr>
<td>0.4666 ± 0.0002</td>
<td>0.5680 ± 0.0002</td>
<td>0.4948 ± 0.0002</td>
<td>90°</td>
<td>This research</td>
</tr>
</tbody>
</table>

with those of other investigators also given in table 1. Further details of the X-ray pattern obtained for both CoWO₄ and NiWO₄ are available elsewhere. (17)

The results of professional chemical analysis for cobalt and tungsten are listed in table 2 for two separate batches. Both the cobalt and tungsten are reported to be low with mole ratio n(Co)/n(W) of (0.978 ± 0.020). If WO₃ were the only impurity present, the mole ratio would be low but the mass percentage of tungsten would exceed the theoretical value for cobalt tungstate, rather than be only 98.8 per cent.

TABLE 2. Composition of transition metal tungstates, MWO₄:

<table>
<thead>
<tr>
<th>Compound and sample</th>
<th>10⁹f(M) a</th>
<th>10⁹f(W) b</th>
<th>n(M)/n(W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoWO₄-II'</td>
<td>18.7 ± 0.03</td>
<td>59.2 ± 0.3</td>
<td>0.986 ± 0.02</td>
</tr>
<tr>
<td>CoWO₄-III' e</td>
<td>18.6 ± 0.3</td>
<td>59.2 ± 0.3</td>
<td>0.978 ± 0.02</td>
</tr>
<tr>
<td>Theoretical</td>
<td>19.21</td>
<td>59.90</td>
<td>1.000</td>
</tr>
<tr>
<td>NiWO₄</td>
<td>21.3 ± 0.3</td>
<td>58.3 ± 0.3</td>
<td>1.14 ± 0.02</td>
</tr>
<tr>
<td>Theoretical</td>
<td>19.15</td>
<td>59.97</td>
<td>1.000</td>
</tr>
</tbody>
</table>

a Cationic metal by titration with EDTA.
c Calorimetric sample.
d Average of three determinations.

of theoretical. A composition of the form (CoWO₄ + xWO₃ + γ), where γ contains neither cobalt nor tungsten, would require 1.6 mass per cent of WO₃ and 1.8 mass per cent of γ to duplicate the analytical results. The sensitivity of the X-ray analysis used is sufficient to rule out such a possibility, so the analytical results must be considered questionable.

To test for the possible presence of volatile impurities (water, etc.) a sample of several mg was heated to 1475 K under a nitrogen atmosphere in a Perkin-Elmer TGS-1 Thermobalance. No mass loss (±0.08) per cent was observed.

The presence of other metal impurities was tested in both batches II' and III' with a Perkin-Elmer 503 Atomic Absorption Spectrophotometer. Trace metals determined (mass fractions: 74 × 10⁻⁶ of cobalt, 524 × 10⁻⁶ of iron, 102 × 10⁻⁶ of
nickel, and $77 \times 10^{-6}$ of zinc) yield an accumulated mass fraction of impurity less than 0.08 per cent so that compounds of these metals do not explain the discrepancy in the bulk analyses.

Atomic absorption spectroscopy was used to determine the mass percentage of cobalt in the sample. The reliability of this determination was low from background noise level within the instrument and problems of preparing consistent standards. Yet the analysis for cobalt gives $(98.7 \pm 0.8)$ mass per cent of the theoretical value. This value, when used with the commercially determined mass percentage of tungsten, gives $n(\text{Co})/n(\text{W}) = (1.00 \pm 0.01)$, close to unity.

**Nickel tungstate.** The sample of “Crystal Grade” nickel tungstate purchased from Alfa Inorganics had been manufactured by Sylvania, Inc. and had a reported purity of 99.96 moles per cent. When the sample was first investigated, it was a light-green amorphous powder. After annealing for 24 h at 1125 K the color changed to pea-green and X-ray exposure for 2 h revealed a pattern of sharp lines. Most lines could be indexed as NiWO$_4$ reflexions but three lines corresponded to reflexions from NiO.$^{(18)}$ A later exposure for 8 h on more sensitive Ilford Type-G film revealed the presence of additional impurity lines in the original material corresponding to reflexions from CaWO$_4$.($^{19}$) and from Na$_2$WO$_4$.($^{20}$) An additional NiO line appeared. However, the presence of the calcium tungstate and sodium tungstate were not known during the purification undertaken to remove the nickel oxide impurity.

The calorimetric sample of NiWO$_4$ was prepared in the following manner. The original material was pressed into a pellet, annealed overnight in a tube furnace at 1050 K, and then crushed in an agate mortar. The powder was poured into a ball mill, distilled water added to make a slurry, and the sample milled for 2 d to crush the powder. After removal from the mill and drying, the sample was forced through a 0.25 mm sieve, boiled for 15 min in 1 M HCl(aq) to leach out NiO. This acid wash changes the color of the sample from dark green to mustard yellow. The material was filtered, rinsed in distilled water, dried, and then given a final annealing at 1170 K for 14 h in a Vycor tube. The color of the sample changed to a dark gold during this annealing. A preliminary X-ray at this point showed the absence of all NiO lines, but very faint WO$_3$ lines persisted. Consequently, the material was boiled in 1 M KOH(aq), filtered, rinsed in distilled water, and dried.

Subsequently, X-ray studies yielded lattice parameters generated from the refined data shown in table 3 which agreed well with those of other investigators. Long-

<table>
<thead>
<tr>
<th>$a$/nm</th>
<th>$b$/nm</th>
<th>$c$/nm</th>
<th>$\beta$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.469 $\pm$ 0.001</td>
<td>0.567 $\pm$ 0.001</td>
<td>0.494 $\pm$ 0.001</td>
<td>90.33°</td>
<td>Broch(19)</td>
</tr>
<tr>
<td>0.460 $\pm$ 0.0015</td>
<td>0.566 $\pm$ 0.002</td>
<td>0.491 $\pm$ 0.002</td>
<td>(90.08 $\pm$ 0.08)°</td>
<td>Keeling(21)</td>
</tr>
<tr>
<td>0.4600 $\pm$ 0.0004</td>
<td>0.5665 $\pm$ 0.0004</td>
<td>0.4912 $\pm$ 0.0004</td>
<td>90°</td>
<td>Swanson et al.(16)</td>
</tr>
<tr>
<td>0.4599 $\pm$ 0.0001</td>
<td>0.5665 $\pm$ 0.0001</td>
<td>0.4910 $\pm$ 0.0001</td>
<td>90°</td>
<td>Sleight(22)</td>
</tr>
<tr>
<td>0.4600 $\pm$ 0.0002</td>
<td>0.5663 $\pm$ 0.0002</td>
<td>0.4911 $\pm$ 0.0002</td>
<td>90°</td>
<td>This research</td>
</tr>
</tbody>
</table>

(Guinier, Cu Kα)
exposure irradiations revealed three impurity lines but no NiO and WO₃ reflexions. Two of these are matched by lines of the α-cristobalite phase of SiO₂ which entered the sample during the final annealing in the Vycor tube. Where the sample had been in contact with the tube, a hard opaque coating formed which, when scraped from the inside of the tube and X-rayed, was observed to be pure α-cristobalite, evidently produced by mineralizing action of NiWO₄ on (amorphous) Vycor. The other impurity line is attributed to the persistent presence of calcium tungstate. The diminished relative abundance of the CaWO₄ in the final sample, as determined by the number and intensity of the X-ray reflexions observed, is attributed to the slight solubility in water of this contaminant and the frequent rinses in distilled water the sample received. The absence of sodium tungstate reflexions is consistent with its higher solubility in water.

The nickel tungstate sample was chemically analyzed for the presence of silicon, calcium, and sodium. The assumption that these contaminants are present as the following compounds, implies impurity levels of 0.56 mass per cent (2.80 moles per cent) of SiO₂, 0.20 mass per cent (0.21 mole per cent) of CaWO₄, and 0.08 mass per cent (0.08 mole per cent) of Na₂WO₄.

The results of chemical analysis for nickel and tungsten are listed in table 2. The value for nickel is high and that for tungsten is low; the calculated mole ratio \( n(\text{Ni})/n(\text{W}) \) is \( 1.14 \pm 0.02 \). Since the X-ray-determined lattice parameters are in such good accord with the previously published values, and since the sensitivity of the X-ray technique is sufficiently great to determine the 0.2 mole per cent of CaWO₄ impurity, this anomalous \( n(\text{Ni})/n(\text{W}) \) mole ratio is not understood.

HEAT-CAPACITY MEASUREMENTS

Heat-capacity measurements in the range 5 to 350 K were made in the Mark II adiabatic cryostat\(^{(21)}\) while those made in the 300 to 500 K range were made in the Mark IV adiabatic thermostat\(^{(22)}\). Relevant loading information for the samples is given in table 4.

**TABLE 4. Calorimeter loading information:**
calorimeter volume \( V \), sample mass \( m \), pressure \( p \) of helium gas, and density \( \rho \) of the sample

\[ \text{Torr} = (101.325/760) \text{kPa} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Calorimeter</th>
<th>( V/\text{cm}^3 )</th>
<th>( m/\text{g} )</th>
<th>( p/\text{Torr} )</th>
<th>( \rho/\text{g cm}^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoWO₄</td>
<td>W-52</td>
<td>59.11</td>
<td>89.1043</td>
<td>63.0</td>
<td>7.76</td>
</tr>
<tr>
<td>NiWO₄</td>
<td>W-30</td>
<td>18.88</td>
<td>43.7491</td>
<td>75.5</td>
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</tr>
<tr>
<td>CoWO₄</td>
<td>W-22-P</td>
<td>84.31</td>
<td>88.3598</td>
<td>55.0</td>
<td>7.76</td>
</tr>
</tbody>
</table>

\( * \) Compare reference 16.
HEAT CAPACITIES

The heat capacities of CoWO₄ are given in Table 5 in chronological sequence so that temperature increments used usually may be inferred from the temperature increments between adjacent determinations, and are expressed in terms of a molar mass.

**Table 5. Heat capacity of cobalt tungstate CoWO₄**

(\(\text{cal}_\text{m} = 4.184 \text{ J}\))

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>(C_p) (cal K(^{-1})mol(^{-1}))</th>
<th>(T) (K)</th>
<th>(C_p) (cal K(^{-1})mol(^{-1}))</th>
<th>(T) (K)</th>
<th>(C_p) (cal K(^{-1})mol(^{-1}))</th>
<th>(T) (K)</th>
<th>(C_p) (cal K(^{-1})mol(^{-1}))</th>
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</thead>
<tbody>
<tr>
<td>303.06</td>
<td>28.62</td>
<td>12.62</td>
<td>0.139</td>
<td>See below</td>
<td></td>
<td></td>
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<tr>
<td>92.84</td>
<td>10.76</td>
<td>99.55</td>
<td>11.71</td>
<td>113.17</td>
<td>13.58</td>
<td>121.92</td>
<td>14.70</td>
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<tr>
<td>130.14</td>
<td>15.71</td>
<td>139.65</td>
<td>16.82</td>
<td>150.35</td>
<td>17.98</td>
<td>160.55</td>
<td>19.01</td>
</tr>
<tr>
<td>170.33</td>
<td>20.25</td>
<td>252.15</td>
<td>25.97</td>
<td>272.67</td>
<td>27.13</td>
<td>292.84</td>
<td>28.62</td>
</tr>
<tr>
<td>211.41</td>
<td>30.33</td>
<td>313.15</td>
<td>34.76</td>
<td>333.14</td>
<td>38.88</td>
<td>353.37</td>
<td>43.12</td>
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<td>221.73</td>
<td>45.33</td>
<td>353.37</td>
<td>47.44</td>
<td>373.14</td>
<td>50.66</td>
<td>392.84</td>
<td>54.88</td>
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<td>241.58</td>
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<td>262.67</td>
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<td>282.72</td>
<td>81.00</td>
<td>452.84</td>
<td>87.20</td>
<td>472.84</td>
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<td>292.84</td>
<td>91.00</td>
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<td>512.84</td>
<td>105.20</td>
<td>532.84</td>
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<td>313.15</td>
<td>105.80</td>
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<td>115.20</td>
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<td>333.14</td>
<td>115.80</td>
<td>572.84</td>
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<tr>
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<td>732.84</td>
<td>191.60</td>
<td>752.84</td>
<td>197.20</td>
<td>772.84</td>
<td>202.60</td>
</tr>
</tbody>
</table>

**Notes:**
- Series I to Series X are listed separately.
- Series XI and XII are listed separately.
- The data are corrected for the enthalpy of fusion.

**Results:**

- The heat capacities of CoWO₄ are given in Table 5.
- The temperature increments used usually may be inferred from the temperature increments between adjacent determinations.
- The heat capacities are expressed in terms of a molar mass.
### TABLE 5—continued

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ΔT (K)</th>
<th>(\langle C_p \rangle) cal K(^{-1}) mol(^{-1})</th>
<th>(C_p) cal K(^{-1}) mol(^{-1})</th>
<th>T (K)</th>
<th>ΔT (K)</th>
<th>(\langle C_p \rangle) cal K(^{-1}) mol(^{-1})</th>
<th>(C_p) cal K(^{-1}) mol(^{-1})</th>
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<tbody>
<tr>
<td></td>
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<td>Series XII (cont.)</td>
<td></td>
<td></td>
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<td>Series XIII</td>
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<tr>
<td>47.60</td>
<td>0.18</td>
<td>7.738</td>
<td>7.744</td>
<td>47.44</td>
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<td>7.592</td>
</tr>
<tr>
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<tr>
<td>47.99</td>
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</tr>
<tr>
<td>48.21</td>
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<td>5.413</td>
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<td>5.010</td>
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<td>0.11</td>
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<td>4.417</td>
<td>4.483</td>
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<td>4.871</td>
<td>4.871</td>
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<tr>
<td>49.45</td>
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<td>49.71</td>
<td>0.25</td>
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of 306.7808 g mol⁻¹; those for NiWO₄ are similarly given in table 6 and are expressed in terms of a molar mass of 306.5576 g mol⁻¹; the enthalpy determinations for both compounds are summarized in table 7. The molar heat capacities for both compounds together with revised values from the heat capacity of ZnWO₄ are presented in figure 2 (5 to 350 K) and figure 3 (300 to 550 K).

### TABLE 6. Heat capacity of nickel tungstate NiWO₄

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### Table Notes:
- **Mark II Cryostat**
- **Series III**
- **Series IV to IX**
- **See below**
- **Series VI**

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### TABLE 7. Enthalpy determinations of cobalt and nickel tungstates, CoWO\(_4\) and NiWO\(_4\), in the Mark II cryostat

(calt\(_{\text{mol}}\) = 4.184 J)

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FIGURE 2. Heat capacities of zinc, nickel, and cobalt tungstates, 5 to 350 K. •, CoWO₄ (Mark II results); ○, NiWO₄ (Mark II results); △, ZnWO₄ (Mark II results); ▲, ZnWO₄ (Mark IV results).

FIGURE 3. Heat capacities of zinc and cobalt tungstates, 300 to 550 K. ■, CoWO₄ (Mark II results); □, CoWO₄ (Mark IV results); ●, ZnWO₄ (Mark II results); ○, ZnWO₄ (Mark IV results).
ADJUSTMENT FOR IMPURITIES

The presence of the separate phase impurities in the nickel tungstate necessitated adjustment of the results in terms of the enthalpies of $\alpha$-cristobalite and calcium tungstate. The thermal functions for silicon dioxide used in the analysis were generated by curve fitting the low-temperature, 5 to 300 K, heat capacities of Westrum (23) which had been extrapolated to 350 K. The adjustment for SiO$_2$ amounted to about 1 per cent below 10 K and about 0.5 per cent over the rest of the temperature region measured. The thermal functions for calcium tungstate used in the analysis for nickel tungstate were generated from the polynomial representation of the low-temperature heat capacities of Lyon and Westrum. (24) The adjustment for separate-phase calcium tungstate was less than 0.1 per cent of the molar heat capacity. Since the mole percentage of the sodium tungstate impurity phase was so low and since data for this compound are available only above 50 K, (25) no adjustment was made to the heat capacity of nickel tungstate for the sodium tungstate phase. Preliminary corrections showed the correction for sodium tungstate to amount to less than 0.05 per cent in regions where reasonable estimates could be made for the heat capacity of sodium tungstate.

THERMOPHYSICAL FUNCTIONS

The experimental molar heat capacities for both samples in non-transition regions (nickel tungstate adjusted for impurities) were fitted to polynomials in temperature by the method of least squares, and integrated to yield values of the thermophysical functions at selected temperature intervals. These derived values are presented in tables 8 and 9 for cobalt and nickel tungstates. Within the transition regions the thermal functions are based upon numerical integration of heat-capacity points mapped on large scale plots.

**TABLE 8. Thermophysical functions of cobalt tungstate CoWO$_4$**

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HEAT CAPACITIES OF NICKEL AND COBALT TUNGSTATES

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The estimated error in the thermodynamic functions of cobalt tungstate is less than 0.1 per cent above 100 K. The error for the thermodynamic functions of nickel tungstate is larger, due to the uncertainty in the mass fractions of the impurity phases. Since the accumulative correction to the molar heat capacity is less than 0.6 per cent, the uncertainty in the thermal functions is still less than 0.2 per cent above 100 K.

The values of the entropy and enthalpy at the lowest temperatures in parentheses in the tables of thermal functions were obtained from plots of \( C_p/T \) against \( T^2 \). For either compound, the magnitude of this extrapolation is negligible. The entropies and Gibbs energies have not been adjusted for nuclear spin or for isotopic mixing contributions and, hence, are practical values for use in chemical thermodynamic calculations.

**Discussion**

**SUPEREXCHANGE INTERACTIONS**

As a consequence of the intensive study of magnetic interactions in insulators, semi-empirical rules, the Goodenough-Kanamori rules (clearly formulated in reviews by Anderson)\(^{26,27}\) have been developed for predicting the sign of the interaction through which magnetic ions couple their moments. When cations occupy octahedral holes in closest-packed anion lattices, e.g. for tungstates and dichlorides,\(^{28}\) the cation–anion–cation angle is 90° and the Goodenough-Kanamori rules predict antiferromagnetic exchange for the iron(II), cobalt, and nickel compounds (compare Goodenough\(^{29}\)). The iron(II), cobalt, and nickel tungstates (and dichlorides) are antiferromagnets in which the spins are ferromagnetically aligned within each layer and the spins in neighboring layers are aligned antiferromagnetically.\(^{30}\) In MnWO\(_4\) (and MnCl\(_2\)), however, the cations do not order ferromagnetically\(^{31}\) within each layer.

Detailed superexchange paths in the tungstates were first discussed by Van Uitert et al.\(^3\) The structure of the tungstates can be thought of as a (distorted) hexagonal closest-packed array of oxygens with the tungsten and metal ions in the octahedral holes, forming independent zigzag chains along the c-axis of the crystal.\(^{32}\) Each W-octahedral chain is attached by common corners to four M-chains and each M-chain is also surrounded by four W-chains. Each M\(^{2+}\) ion can interact by 90° superexchange with its two nearest neighbors in the chain, with which it shares two oxygen atoms each. There is also the possibility of next-nearest neighbor exchange within the chains, involving the tungsten atoms in an adjacent octahedron. Inter-chain coupling is possible both between layers and within the same layer by exchange paths of the type M–O–W–O–M, where all the angles involved are close to 90°. These interlayer interactions should be large, since the results of Lesne and Caillet\(^{33}\) predict that the strongest bonding paths are between layers. Since the exchange interaction is enhanced with bond strength, the interlayer exchange interaction should be significant. Superexchange interactions of the type M–O–W–O–M have been studied in the ordered perovskites by Blasse\(^{34}\) and found to be comparable in strength to those in the tungstates.
MAGNETIC BEHAVIOR

Susceptibilities of the tungstates\(^{(3-5)}\) show characteristic maxima associated with antiferromagnetic phase changes. Since magnetic moments of the iron, cobalt, and nickel ions are all in excess of expectation for a spin-only model, considerable orbital angular momentum is retained by the ions within their low-symmetry crystal fields. Calculations predicting the amount retained involve lengthy considerations of the low-symmetry distortions of the octahedral fields and the magnitudes of the spin–orbit coupling. Cobalt tungstate is the only tungstate for which this calculation has been done. The authors, Zvyagin and Khats'ko\(^{(9)}\) were able to calculate susceptibilities and magnetic moments from their assigned energy levels in good accord with their experimental values.

Also significant is the discrepancy between the paramagnetic Curie temperatures \(\Theta_p\) derived from susceptibility measurements in the low-temperature region and the high-temperature (290 to 700 K) measurements of Shapovalova et al.\(^{(4)}\) which yield positive \(\Theta_p\)'s for ferrous and cobalt tungstate. These positive \(\Theta_p\)'s are indicative of ferromagnetic interactions within the crystal, even though the materials are known to be antiferromagnetic. Since in cobalt and iron(II) tungstate the ions in the \(bc\) plane are aligned ferromagnetically, with adjacent planes aligned antiferromagnetically, the high-temperature determination of susceptibility may reflect the dominance of the intralayer exchange. This type of behavior is known to exist in the transition-metal dichlorides where adjacent planes of ferromagnetic ions are aligned antiferromagnetically. The strong intralayer ferromagnetic interaction leads to positive paramagnetic Curie temperatures even at low temperatures. As pointed out by Dachs\(^{(12)}\) molecular-field theory leads to the relation:

\[
\frac{|\Theta_p|}{T_n} = \frac{\Sigma J_{ij}}{2\Sigma J_{ij} S_i S_j}.
\]

In \(\text{MnWO}_4\), the near-neighbor antiferromagnetic coupling leads to the cancellation of terms in the denominator, producing a large ratio (5.5). The ferromagnetic planes in the \(\text{FeWO}_4\), \(\text{CoWO}_4\), and \(\text{NiWO}_4\) do not produce such cancellations and the ratios are significantly lower, (0.3, 1.8, and 0.8, respectively).

SPECIAL INFORMATION

Several investigations have been made of the electronic energy levels of pure and of doped diamagnetic tungstates. Study of the latter was undertaken with the intention of eliminating exchange effects.

In studies on the pure tungstates, Ferguson and others\(^{(35, 36)}\) measured the absorption spectra of \(\text{CoWO}_4\) and \(\text{NiWO}_4\).

As discussed by Lyon\(^{(37)}\) the crystal-field splittings are 25 and 18 per cent less for the \(\text{Co}^{2+}\) and \(\text{Ni}^{2+}\) ions in the tungstate than when they are octahedrally coordinated in the diamagnetic oxide \(\text{MgO}\).\(^{(35, 36)}\) Such a decrease is sufficient to alter the expected colors of the samples. Whereas octahedrally coordinated cobalt and nickel compounds in solution are usually pink and green, the respective tungstates are blue and mustard yellow. These decreases in crystal-field splitting are attributed to the electron-withdrawing power of the \(\text{W}^{6+}\) ion, as mentioned by Lyon\(^{(37)}\) and
also by Shannon and Vincent(38) in their discussion of covalency in the tungstates. This large effect by the tungsten ion makes the superexchange path involving the tungsten important.

The optical absorption spectra of Ni$^{2+}$ ion in ZnWO$_4$ has been studied by Reynolds et al. In an octahedral field the ground state of Ni$^{2+}$ is a singlet, which will not split under a crystal field of lower symmetry. Reynolds et al. found this $^3A_2$ term to lie more than 6000 cm$^{-1}$ below the first excited $^3T_2$(E) term. Still, the spin-orbit coupling in the nickel ion must reintroduce orbital angular momentum into the ground states, since the effective magnetic moments exceed the spin-only prediction. However, no information is available as regards these energy states. The assignment of the lowest levels for Co$^{2+}$ ions in diamagnetic tungstate matrices has been accomplished by Atsarkin et al. for Co$^{2+}$ : MgWO$_4$, and by Zvyagin and Khats'ko, and by Bates and co-workers, for Co$^{2+}$ : ZnWO$_4$. Atsarkin et al. measured the optical absorption spectra of the cobalt ions in MgWO$_4$ (0.01 mass per cent of Co$^{2+}$) at 300 K. They were able to interpret the spectra observed without considering either the orthorhombic components of the crystal field or the non-centrosymmetric location of the cobalt ions. They used the crystal-field parameters derived from the spectra to calculate the splitting of the lowest triplet state into six Kramers doublets by the spin-orbit interaction. Zvyagin and Khats'ko use the results of e.p.r. studies of Co$^{2+}$ : ZnWO$_4$ as well as their own measurements of the single-crystal magnetic susceptibilities to assign energy levels to the six Kramers doublets. The agreement with the results of Atsarkin et al. is reasonable. Bates et al. have also studied the e.p.r. spectrum of Co$^{2+}$ : ZnWO$_4$ and assigned energies to the six doublets on the basis of their results. The agreement with the results of Zvyagin and Khats'ko is excellent.

An additional estimate of the wavenumber interval $\Delta$ separating the ground-state doublet from the first excited doublet of Co$^{2+}$ in ZnWO$_4$ has been given by Galkin et al. They interpret their measurements of the broadening of the e.p.r. line in terms of spin-lattice relation times with a value $\Delta = (230 \pm 30)$ cm$^{-1}$.

**SCHOTTKY ANOMALIES AND MAGNETIC TRANSFORMATION**

Using the standard formulas for heat capacity as a function of energy levels, it is possible to calculate the expected Schottky-type behavior in the heat capacity of cobalt tungstate. Beginning at about 60 K, the heat capacity should rise to a maximum of about 1.35 cal, K$^{-1}$ mol$^{-1}$ at a temperature of 200 K, then drop 10 per cent by 300 K, after which it should slowly rise towards the maximum as the temperature increases beyond 500 K.

Since the ground state of nickel tungstate is an orbital singlet, the magnetic entropy to be obtained will simply be $R \ln(2S+1) = R \ln 3$. At the transition temperature of cobalt tungstate (for which only the lowest Kramers doublet is thermally populated) the expected entropy change associated with the antiferromagnetic ordering would be $R \ln 2$ similar to the behavior of cobalt in CoF$_2$ and CoCl$_2$. In addition, there should be further contributions to the entropy attributed to the population of the higher-lying doublets.
RESOLUTION OF MAGNETIC AND LATTICE CONTRIBUTIONS

In the preliminary step, the Debye characteristic temperatures $\Theta_D$ were calculated for each experimental point for tungstate including zinc tungstate. The curve for $\Theta_D$ of zinc tungstate behaves normally. The other two curves have regions where the values are anomalously low; these correspond to the regions of large magnetic contributions to the heat capacity. Ratios of the $\Theta_D$'s: $\Theta_D(\text{CoWO}_4)/\Theta_D(\text{ZnWO}_4)$ and $\Theta_D(\text{NiWO}_4)/\Theta_D(\text{ZnWO}_4)$ were calculated as a function of temperature. For these compounds, the ratios below 100 K reflect the magnetic contributions to the heat capacity.

Assessment of the low-temperature $\Theta_D$, and subsequently the low-temperature heat capacity, involves a complication due to the presence of the excited state in the cobalt ion because the Schottky contributions to the heat capacity of cobalt tungstate lower the observed $\Theta_D$'s. To determine the lattice heat capacity, Schottky heat capacities were generated from the spectroscopic data of Co$^{2+}$ ions in MgWO$_4$ (Co$^{2+}$:MgWO$_4$) and Co$^{2+}$ ions in ZnWO$_4$ (Co$^{2+}$:ZnWO$_4$). These heat capacities were then subtracted from the experimental heat capacities and the $\Theta_D$'s calculated for the resulting values. Since the harmonic approximation predicts $\Theta_D(\text{CoWO}_4)/\Theta_D(\text{ZnWO}_4) = \{M(\text{Zn})/M(\text{Co})\}^{1/2} = 1.053$, the estimated curve was drawn to this value as a lower limit. The molar masses of the ions rather than of the molecules were used since the heavy tungsten atoms form a matrix in which the first-row metals oscillate. Such behavior has been seen in the studies of iron impurities in metal host lattices. Additional evidence for such a limit is the valence-force-field calculation of Lesne and Caillet which showed the strongest bonds within the crystal were between W and O; the metal ions are bound relatively weakly to the oxygens. Hence, at temperatures greater than 100 K, the estimated curve was smoothly interpolated between the two calculated curves.

A simple mass adjustment of $\Theta_D$ does not suffice for a lattice estimate of nickel tungstate. As can be seen in figure 2, above 60 K, the heat capacity of zinc tungstate is greater than that of nickel tungstate. A mass adjustment does little to this difference.

Similar behavior has been seen previously in the study of the metal difluorides by Stout and Catalano. When the heat capacity of ZnF$_2$ is simply subtracted from that of NiF$_2$, the remaining heat capacity is significantly negative for several hundred kelvins. Stout and Catalano assumed the vibrational contributions to the entropy and heat capacity of the difluorides obey a law of corresponding states, scaling as the parameter $(T/T_m)$, where $T_m$ is the melting temperature. Such an assumption was necessary to take proper account of the large differences between the melting temperatures of the zinc and nickel difluorides.

Since the reported melting temperatures of NiWO$_4$: 1663 K, 1723 K, are higher than that of ZnWO$_4$: 1474 K and of all other tungstates, the lattice estimate must take the melting-temperature differences into consideration. The relation chosen between the $\Theta_D$ of nickel and zinc tungstates was the Lindemann melting formula which indicates the melting temperature $T_m$ to be proportional to...
to such structural factors as ionic masses, sizes of unit cell, and $\Theta_D$ each to appropriate powers:

$$T_m \propto \Theta_D^2 V^{2/3} M,$$

The low-temperature limit of the ratio of the $\Theta_D$'s of nickel and zinc tungstate was then taken as

$$\frac{\Theta_D(NiWO_4)}{\Theta_D(ZnWO_4)} = \left[ \frac{T_m(Ni)\{V(Zn)\}^{2/3} M(Zn)}{T_m(Zn)\{V(Ni)\}^{2/3} M(Ni)} \right]^{1/2} = 1.133.$$

The lowest limit was then joined to the experimental ratio of the ratio $\Theta_D(NiWO_4)/\Theta_D(ZnWO_4)$ at 150 K. The estimated $\Theta_D(NiWO_4)$ lattice heat capacities were then calculated from the Debye equation and the estimated Debye $\Theta_D$'s.

**EXCESS HEAT CAPACITIES OF NiWO$_4$ AND CoWO$_4$**

The heat capacities of these tungstates and the estimated lattice heat capacities in the vicinity of the transition temperatures are shown in figure 4 together with the zinc tungstate values used for comparison with the lattice contribution. To determine the excess entropies and enthalpies, the differences between the pairs of curves were integrated. The resulting entropy and enthalpy of transition for nickel tungstate are

$$\Delta S_{mag} = 2.06 \text{ cal}_\text{th} K^{-1} \text{ mol}^{-1}, \quad \Delta H_{mag} = 100.2 \text{ cal}_\text{th} \text{ mol}^{-1}.$$

A graph of magnetic entropy for nickel tungstate is shown in figure 5(a). The entropy obtained corresponds to 94 per cent of $R \ln 3$.

The existence of a discrepancy between the expected and experimental entropies cannot be considered surprising, in view of the crudeness of the lattice approximation. Even assuming the Lindemann melting relation to be valid, the $\Theta_D$ ratio curve chosen
HEAT CAPACITIES OF NICKEL AND COBALT TUNGSTATES

was selected as reasonable, but is certainly not definitive. One indication of probable error in the assignment of the lattice is the fraction of entropy appearing above the Néel temperature. In three-dimensional magnetic systems, this entropy is often greater than 30 per cent of the total and continues to appear at $3T_N$. For the nickel tungstate only 18 per cent appears above $T_N$. However, within the uncertainties present, the total entropy is considered as evidence for the expected spin-disorder transition in nickel tungstate.

The excess entropy and enthalpy of cobalt tungstate were calculated from the difference of the total and estimated lattice curves shown in figure 4(b) on which the heat capacity of zinc tungstate is also shown. The excess entropy is displayed in figure 5(b). The entropy approaches $R \ln 2$; then the Schottky contribution to the heat capacity causes the entropy to rise again. Nevertheless, the magnetic entropy associated with the antiferromagnetic transition is clearly $R \ln 2$, not the $R \ln 4$ predicted from the spin-only model. The entropy above $T_N$, associated with magnetic short-range order, cannot be directly evaluated but the difference between $R \ln 2$ and the entropy which has appeared by $T_N$ is 23 per cent of $R \ln 2$.

The excess heat capacities of cobalt and nickel tungstates show antiferromagnetic spin-wave contributions at low temperatures, as can be seen in figure 6. From considerations of mass and volume, the lattice heat capacities of nickel and cobalt tungstate should be lower than the heat capacity of zinc tungstate. The fact that the heat capacities are larger, while still proportional to $T^3$, demonstrates the existence of spin-wave heat capacities for these compounds. Interestingly enough, nickel tungstate has the same initial slope as cobalt tungstate even though its transition temperature is 13 K higher.

Although iron(II), cobalt, and nickel tungstates consist of ferromagnetic layers aligned antiferromagnetically, there is no evidence for two-dimensional magnetic behavior in the tungstates. In $K_2NiF_4$, $K_2MnF_4$, and $MnTiO_3$ anomalies in the susceptibilities have been interpreted as indicative of two-dimensional ordering, e.g. more than 45 per cent of the magnetic entropy of $MnTiO_3$ appears above the Néel temperature. However, these three compounds all display antiferromagnetic

![Figure 5](image-url)  
**FIGURE 5.** (a), (b) Magnetic entropies of (a) nickel tungstate and (b) cobalt tungstate.
coupling within the layers, unlike the FeWO$_4$, CoWO$_4$, and NiWO$_4$. The absence of such characteristic behavior in the susceptibilities of any of the tungstates and the relatively low percentages of short-range entropy herald essentially three-dimensional exchange properties.

REFERENCES

11. Eremenko, V. V. Personal communication (1975).
HEAT CAPACITIES OF NICKEL AND COBALT TUNGSTATES