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The Spinels $CuCr_2O_4$ and $CuRh_2O_4$

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Abstract

Rietveld refinement of X-ray powder data measured for $CuCr_2O_4$ [copper(II) dichromium(III) tetraoxide] and $CuRh_2O_4$ [copper(II) dirhodium(III) tetraoxide] indicates that their structures at room temperature are centrosymmetric, $I4_1/amd$, rather than as previously reported, noncentrosymmetric $I\bar{4}2d$. Trial refinement in $I\bar{4}2d$ shows insignificant improvement in the agreement between observed and calculated intensities, and no statistically significant deviation from a centrosymmetric structure.

Comment

With sufficient concentration of non-spherical, so-called Jahn–Teller (JT) ions, such as Cu^{2+} or Mn^{3+}, the normally cubic $Fd3m$ spinel structure may undergo a cooperative distortion to a tetragonal structure with either an elongated or compressed unit cell. A search of the Inorganic Crystal Structure Database (Bergerhoff, Hundt, Sievers & Brown, 1983) shows that all elongated JT spinels for which $c > a$ have the Mn_3O_4 hausmannite structure with space group $I4_1/amd$. However, all compressed JT spinels with $c < a$ are reported to have space group $I\bar{4}2d$, a noncentrosymmetric subgroup of $I4_1/amd$. Only two members of the $c < a$ group have been reported: $CuCr_2O_4$ and $CuRh_2O_4$.

The room-temperature crystal structure of copper chromium spinel (Prince, 1957) was assigned the noncentrosymmetric space group $I\bar{4}2d$ over the centrosymmetric alternative, $I4_1/amd$, on the basis of a reported qualitatively better agreement between the ten observed and calculated neutron diffraction intensities. The identical $I\bar{4}2d$ structure was adopted for copper rhodium spinel (Dulac, 1969) without further discussion of the choice of space group.

A restudy of these two spinels using Rietveld refinement of X-ray powder diffraction data is reported here. Initial refinement in the previously suggested noncentrosymmetric space group yielded deviations from a centrosymmetric structure that were much smaller than those reported by Prince (1957) and Dulac (1969), prompting trial refinement in the corresponding centrosymmetric space group. For $CuCr_2O_4$, the pertinent R factors are: $R_p = 0.0279$, $R_{wp} = 0.0368$ and $R_B = 0.0387$ for a centrosymmetric model, and $R_p = 0.0279$, $R_{wp} = 0.0369$ and $R_B = 0.0385$ for the noncentrosymmetric case. Similarly, for $CuRh_2O_4$ these R factors are: $R_p = 0.0440$, $R_{wp} = 0.0603$ and $R_B = 0.0469$ for the centrosymmetric case, and $R_p = 0.0439$, $R_{wp} = 0.0603$ and $R_B = 0.0467$ for the noncentrosymmetric case. Due to the increased number of (atom position) variables, some small apparent improvement may be expected with an noncentrosymmetric model, but the differences here are seen to be minor.

The two additional positional parameters, x(Cr,Rh) and x(O), in $I\bar{4}2d$ refined to within 2.9 and 0.1 standard uncertainties of their symmetry-fixed $I4_1/amd$ values in the chromium spinel, and to within 2.2 and 0.6 standard uncertainties in the rhodium spinel. Furthermore, with a second, but less extensive, data set measured on the same rhodium spinel sample, the Rh and O positional variables refined to within 0.6 and 1.8 standard uncertainties of the centrosymmetric fixed values. Taken together, these data demonstrate that the apparent deviations from a centrosymmetric structure are not statistically significant and that the correct space group is, in both cases, $I4_1/amd$.

Trial refinement of the tetrahedral and octahedral site occupancies revealed no detectable deviation from full occupancy of Cu in the tetrahedral sites of both structures and full occupancy of Cr (or Rh) in the octahedral sites. Both may be therefore classified as normal spinels.

The refined atomic positional parameters for the centrosymmetric space group are given in Tables 1 and

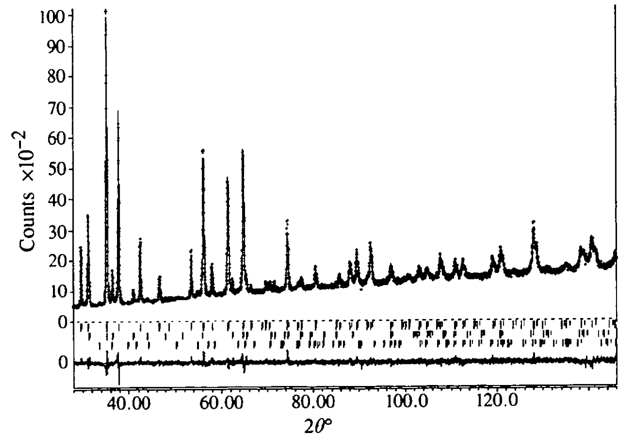

Fig. 1. Observed (crosses), calculated (solid line) and difference profiles from Rietveld analysis of the chromium spinel sample. Tick marks indicate the positions of the allowed reflections for $CuCr_2O_4$ (upper), $CuCrO_2$ (middle), and Cr_2O_3 (lower).

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4. All standard uncertainties quoted are corrected for the effect of serial correlation of the data (Bérar & Lelann, 1991). The refined cell dimensions are in satisfactory agreement with the most recent literature values: a = 6.0336 (3), c = 7.7824 (6) Å for $CuCr_2O_4$ (Morris *et al.*, 1984) and a = 6.175, c = 7.902 Å for $CuRh_2O_4$ (Powder Diffraction File No. 41-402).

Interatomic distances and angles are listed for comparison. In common *Fd*3*m* spinels, the tetrahedral site is regular, while in these spinels the Jahn–Teller effect is expressed as a considerable flattening of the CuO_4 tetrahedron along the c axis (see Fig. 3). The width-to-height ratio of the CuO_4 coordination polyhedron is 1.26 in $CuCr_2O_4$ and 1.33 in $CuRh_2O_4$. This distortion is produced by a (less severe) flattening of the unit cell, coupled with movement of the O atoms in such a manner as to increase the CuO_4 group distortion while keeping the CrO_6 or RhO_6 octahedra quite regular. The cell distortion results in a slightly closer approach of nearest Cr (or Rh) atoms along some of the chains of octahedra. This is more destabilizing with a smaller cell and probably accounts for the Jahn–Teller distortion being slightly less in the chromium spinel than in the larger-volume rhodium spinel.

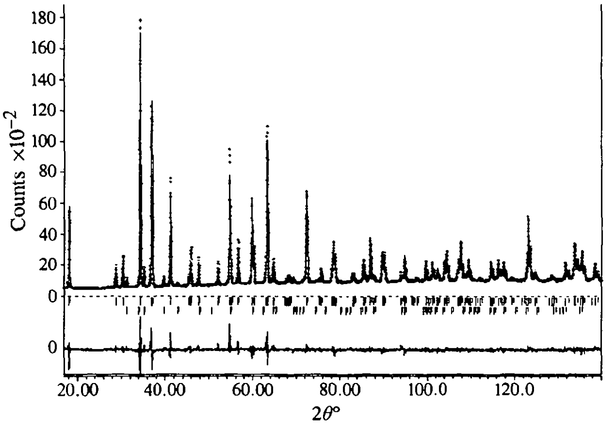

Fig. 2. Observed (crosses), calculated (solid line) and difference profiles from Rietveld analysis of the rhodium spinel sample. Tick marks indicate the positions of the allowed reflections for $CuRh_2O_4$ (upper), and $CuRhO_2$ (lower).

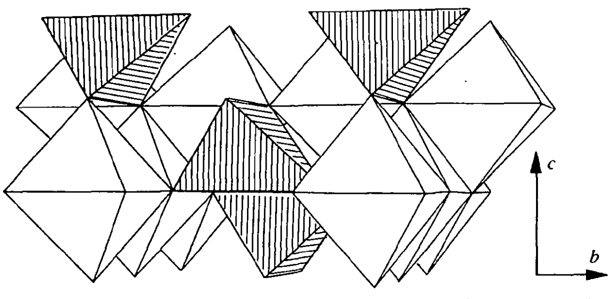

Fig. 3. $CuCr_2O_4$ viewed nearly along the a axis showing the compressed CuO_4 tetrahedra and the chains of edge-sharing CrO_6 octahedra.

Restudy of these spinels concludes that simple axially symmetric distortion of the spinel structure lowers the symmetry from *Fd*3*m* to *I*4$_1$/*amd* irrespective of whether the sites are axially compressed or axially extended. The particular choice of space group is also significant in assigning the symmetry of JT spinels further transformed by lowering of temperature or by solid solution (Armbruster, Lager, Ihringer, Rotella & Jorgensen, 1983; Ivanov & Talanov, 1995).

Experimental

$CuCr_2O_4$ was prepared by heating a pressed pellet of a mixture of Cr_2O_3 and CuO in air for 68 h at 1173 K. A minor amount of Cu^{2+} is reduced under this oxygen fugacity producing $CuCrO_2$ and Cr_2O_3, measured by Rietveld refinement to constitute 6% and 2% of the sample, respectively. The remaining 92% is $CuCr_2O_4$. Rh_2O_3, prepared from rhodium nitrate, was mixed with CuO, pressed into a pellet and heated at 1373 K in a vertical tube furnace under flowing O_2 for *ca* 96 h to prepare the $CuRh_2O_4$ sample. Minor reduction of Cu^{2+} produced $CuRhO_2$, measured by Rietveld refinement to constitute 4% of the sample. No Rh_2O_3 was detected. The remaining 96% is $CuRh_2O_4$.

$CuCr_2O_4$

Crystal data

$CuCr_2O_4$
M_r = 231.55
Tetragonal
*I*4$_1$/*amd*
a = 6.0341 (4) Å
c = 7.7888 (6) Å
V = 283.60 (4) Å^3
Z = 4
D_x = 5.43 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54184 Å
θ = 14–73°
μ = 70.7 mm^{-1}
T = 295 K
15 × 12 × 0.1 mm
Brown

Data collection

Philips diffractometer
$\theta/2\theta$ scans
Specimen mounted in reflection mode

$2\theta_{\rm min}$ = 28°
$2\theta_{\rm max}$ = 146°
Increment in 2θ = 0.025°

Refinement

R_p = 0.028
R_{wp} = 0.037
$R_{\rm exp}$ = 0.027
R_B = 0.039
Excluded region(s): none
Profile function: pseudo-Voigt

22 parameters
$(\Delta/\sigma)_{\rm max}$ = 0.10
Preferred orientation correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic displacement parameters (Å^2) for $CuCr_2O_4$*

	x	y	z	$U_{\rm iso}$
Cu	0	1/4	7/8	0.006 (2)
Cr	0	1/2	1/2	0.003 (2)
O	0	0.4672 (9)	0.2480 (7)	0.001 (2)

Table 2. *Selected geometric parameters (Å, °) for* $CuCr_2O_4$

$Cu—O^{i}$	1.957 (5) × 4	$Cr—O^{ii}$	1.999 (4) × 4
Cr—O	1.973 (5) × 2		
$O^{i}—Cu—O^{iii}$	121.4 (1)	$O—Cr—O^{ii}$	86.1 (3)
$O^{i}—Cu—O^{iv}$	103.9 (5)	$O—Cr—O^{v}$	93.9 (3)
$O^{v}—Cr—O^{vi}$	82.0 (2)	$O^{ii}—Cr—O^{vi}$	98.0 (2)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $y-\frac{1}{4}, \frac{1}{4}-x, \frac{3}{4}-z$; (iii) $x, y-\frac{1}{2}, 1-z$; (iv) $y-\frac{3}{4}, \frac{1}{4}+x, \frac{3}{4}+z$; (v) $\frac{1}{4}-y, \frac{3}{4}+x, \frac{1}{4}+z$; (vi) $y-\frac{1}{4}, \frac{3}{4}+x, \frac{1}{4}+z$.

Table 3. *Contact distances (Å) for* $CuCr_2O_4$

$Cr\cdots Cr^{i}$	2.8884 (2)	$Cr\cdots Cr^{ii}$	3.0170 (2)

Symmetry codes: (i) $y-\frac{1}{4}, \frac{1}{4}-x, \frac{3}{4}-z$; (ii) $x, y-\frac{1}{2}, 1-z$.

$CuRh_2O_4$

Crystal data

$CuRh_2O_4$
$M_r = 333.36$
Tetragonal
$I4_1/amd$
$a = 6.1756$ (5) Å
$c = 7.9006$ (6) Å
$V = 301.31$ (4) Å^3
$Z = 4$
$D_x = 7.35$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
$\theta = 9$–70°
$\mu = 96.8$ mm^{-1}
$T = 295$ K
15 × 12 × 0.1 mm
Black

Data collection

Philips diffractometer
$\theta/2\theta$ scans
Specimen mounted in reflection mode

$2\theta_{\min} = 17°$
$2\theta_{\max} = 140°$
Increment in $2\theta = 0.025°$

Refinement

$R_p = 0.044$
$R_{wp} = 0.060$
$R_{\rm exp} = 0.028$
$R_B = 0.047$
Excluded region(s): none
Profile function: pseudo-Voigt

20 parameters
$(\Delta/\sigma)_{\max} = 0.10$
Preferred orientation correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 4. *Fractional atomic coordinates and isotropic displacement parameters (Å^2) for* $CuRh_2O_4$

	x	y	z	$U_{\rm iso}$
Cu	0	1/4	7/8	0.016 (2)
Rh	0	1/2	1/2	0.010 (2)
O	0	0.4693 (15)	0.2413 (13)	0.015 (2)

Table 5. *Selected geometric parameters (Å, °) for* $CuRh_2O_4$

$Cu—O^{i}$	1.962 (8) × 4	$Rh—O^{ii}$	2.055 (7) × 4
Rh—O	2.053 (8) × 2		
$O^{i}—Cu—O^{iii}$	124.2 (2)	$O—Rh—O^{ii}$	87.9 (5)
$O^{i}—Cu—O^{iv}$	102.7 (8)	$O—Rh—O^{v}$	92.1 (3)
$O^{v}—Rh—O^{vi}$	82.5 (3)	$O^{ii}—Rh—O^{vi}$	97.5 (3)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $y-\frac{1}{4}, \frac{1}{4}-x, \frac{3}{4}-z$; (iii) $x, y-\frac{1}{2}, 1-z$; (iv) $y-\frac{3}{4}, \frac{1}{4}+x, \frac{3}{4}+z$; (v) $\frac{1}{4}-y, \frac{3}{4}+x, \frac{1}{4}+z$; (vi) $y-\frac{1}{4}, \frac{3}{4}+x, \frac{1}{4}+z$.

Table 6. *Contact distances (Å) for* $CuRh_2O_4$

$Rh\cdots Rh^{i}$	2.9442 (3)	$Rh\cdots Rh^{ii}$	3.0878 (3)

Symmetry codes: (i) $y-\frac{1}{4}, \frac{1}{4}-x, \frac{3}{4}-z$; (ii) $x, y-\frac{1}{2}, 1-z$.

For both compounds, program(s) used to refine structures: *DBWS*-9411 (Young, Sakthivel, Moss & Paiva-Santos, 1994); molecular graphics: *ATOMS* (Dowty, 1989).

Lists of powder diffraction intensity data have been deposited with the IUCr (Reference: BR1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Pentaamminechlorocobalt(III) Hydroxotetranitronitrosylruthenate(III)

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Abstract

The structure of $[CoCl(NH_3)_5][Ru(NO_2)_4(OH)(NO)]$ consists of octahedral $[CoCl(NH_3)_5]^{2+}$ and $[Ru(NO_2)_4(OH)(NO)]^{2-}$ ions. These units are held together *via* a three-dimensional network of intermolecular O—H···O, N—H···O and N—H···Cl hydrogen bonds.