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sites of space group $C2/m$, the magnetic moments in the antiferromagnetic ground states are aligned parallel to [100] for the 4i site and to [010] for the 4h site in α-FeMoO$_4$, but parallel to [001] for both sites in α-CoMoO$_4$. Therefore, highly competing interactions with respect to the orientation of the magnetic moments are expected for the mixed compositions.
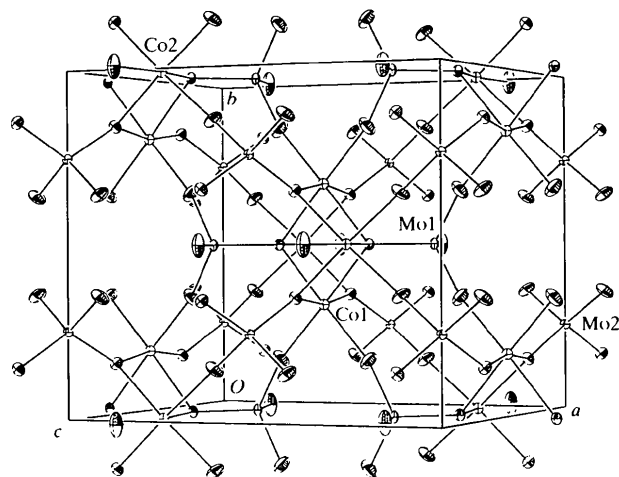
A mixed transition metal molybdate, β-(Co₀.₇Fe₀.₃)MoO₄

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Abstract

The high-temperature modification of the title mixed compound, cobalt iron molybdate, a transition metal molybdate of type β-AMoO$_4$, with A = (Co$_{0.7}$Fe$_{0.3}$), is metastable at room temperature. The distribution of Fe and Co is different for the two non-equivalent A sites: only 18 (9)% of all atoms on the 4i site are Fe, compared with 43 (9)% on the 4h site.

Comment

For the transition metal molybdates AMoO$_4$, with A = Fe or Co, three different modifications were reported by Sleight & Chamberland (1968), i.e. the high-pressure form AMoO$_4$-II, the standard modification α-AMoO$_4$ and the high-temperature phase β-AMoO$_4$. The reversible phase transition between the α- and β-phases takes place at about 673 K for A = Fe and at about 773 K for A = Co. Motivated by the very different magnetic behaviour of α-FeMoO$_4$ and α-CoMoO$_4$ (Ehrenberg et al., 1994), we have studied compounds of mixed composition. For the Co:Fe ratio of 0.7:0.3, we have obtained the title β-modification at room temperature, which is at least metastable under ambient conditions. The crystal structure of this β-modification is only known from α-MnMoO$_4$ (Abrahams & Reddy, 1965). It has not been refined for β-FeMoO$_4$ and β-CoMoO$_4$.

The Co:Fe ratio is different for the two non-equivalent A sites: 18 (9)% of all atoms on the 4i site are Fe, compared with 43 (9)% on the 4h site. This is of importance for the magnetic properties of the mixed compounds. In the case of the α-phases, in which the transition metal ions also occupy the 4h and 4i

Fig. 1. The crystal structure of the title β-AMoO$_4$ compound. All cations within one unit cell are shown with their complete coordination sphere, i.e. [MoO₄] tetrahedra and [AO₆] octahedra. For brevity, the mixed A sites are labelled Co1 and Co2. Displacement ellipsoids are shown at the 50% probability level.

Experimental

The title compound was prepared by subsolidus reaction of a mixture of MoO₃ (99.99%, Aldrich), Co₃O₄ (99.99%, Aldrich), CoO (99.9%, Aldrich), Fe₂O₃ (99.98%, Aldrich) and Fe (99.9%, Aldrich) in the ratio 1:0.175:0.175:0.1:0.1. The reactants were mixed intimately in an agate mortar under acetone, sealed in an evacuated silica tube and heated to 1273 K at a rate of 300 K h^{-1}. After 10 h, the reaction product was cooled down, first at a rate of 40 K h^{-1} to 873 K, then at a rate of 15 K h^{-1} to 723 K and finally to room temperature at a rate of 18 K h^{-1}.

Crystal data

Co₀.₇Fe₀.₃MoO₄	Mo $K\alpha$ radiation
M_r = 217.54	λ = 0.71093 Å
Monoclinic	Cell parameters from 25
$C2/m$	reflections
a = 10.221 (3) Å	θ = 6.04–16.69°
b = 9.275 (3) Å	μ = 8.79 mm^{-1}
c = 7.024 (2) Å	T = 299 (2) K
β = 106.87 (2)°	Prism
V = 637.2 (3) Å^3	0.075 × 0.050 × 0.037 mm
Z = 8	Dark brown
D_x = 4.546 Mg m^{-3}	
D_m not measured	

Data collection

Nonius CAD-4 diffractometer	$R_{int} = 0.052$
$\omega/2\theta$ scans	$\theta_{max} = 35°$
Absorption correction:	$h = -16 \rightarrow 16$
ψ scan (North *et al.*, 1968)	$k = 0 \rightarrow 14$
	$l = -11 \rightarrow 11$
$T_{min} = 0.494$, $T_{max} = 0.667$	3 standard reflections
2928 measured reflections	frequency: 120 min
1469 independent reflections	intensity decay: 2.0%

Refinement

Refinement on F^2	$\Delta\rho_{max} = 2.168$ e $Å^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.037$	(at 0.62 Å from Mo2)
$wR(F^2) = 0.095$	$\Delta\rho_{min} = -1.759$ e $Å^{-3}$
$S = 1.135$	(at 0.66 Å from Mo1)
1469 reflections	Extinction correction:
65 parameters	*SHELXL93* (Sheldrick,
$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2$	1993)
$+ 2.6794P]$	Extinction coefficient:
where $P = (F_o^2 + 2F_c^2)/3$	0.0006 (3)
$(\Delta/\sigma)_{max} < 0.001$	Scattering factors from
	International Tables for
	Crystallography (Vol. C)

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

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Mo1	0.27128 (5)	0	0.40442 (8)	0.00776 (13)
Mo2	1/2	0.24850 (6)	0	0.00722 (13)
Co1†	1/2	0.32151 (10)	1/2	0.0080 (2)
Fe1‡	1/2	0.32151 (10)	1/2	0.0080 (2)
Co2§	0.19949 (9)	0	-0.14440 (13)	0.0077 (2)
Fe2¶	0.19949 (9)	0	-0.14440 (13)	0.0077 (2)
O1	0.3662 (4)	0.1562 (5)	0.4720 (7)	0.0234 (8)
O2	0.1415 (5)	0	0.5393 (7)	0.0090 (8)
O3	0.4576 (3)	0.3472 (4)	0.1959 (5)	0.0109 (6)
O4	0.3577 (4)	0.1440 (4)	-0.1093 (6)	0.0187 (7)
O5	0.2016 (6)	0	0.1458 (8)	0.0230 (13)

† Site occupancy = 0.57 (9). ‡ Site occupancy = 0.43 (9). § Site occupancy = 0.82 (9). ¶ Site occupancy = 0.18 (9).

Table 2. *Selected bond lengths (Å)*

Mo1—O1	1.731 (4)	Co1—O3^{iii}	2.066 (3)
Mo1—O1^i	1.731 (4)	Co1—O3	2.066 (3)
Mo1—O5	1.748 (6)	Co1—O2^{iv}	2.163 (3)
Mo1—O2	1.841 (5)	Co1—O2^v	2.163 (3)
Mo2—O4	1.731 (4)	Co2—O5	2.032 (6)
Mo2—O4^{ii}	1.731 (4)	Co2—O4	2.057 (4)
Mo2—O3	1.807 (3)	Co2—O4^i	2.057 (4)
Mo2—O3^{ii}	1.807 (3)	Co2—O3^{vi}	2.093 (4)
Co1—O1	2.026 (4)	Co2—O3^{vii}	2.093 (4)
Co1—O1^{iii}	2.026 (4)	Co2—O2^{viii}	2.126 (5)

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

The occupancy factors for Co and Fe were refined as least-squares parameters with the sum for each site constrained to be 1, but without constraints for the overall Co:Fe ratio.

Data collection: *CAD-4 Diffractometer Control Software* (Nonius, 1993). Cell refinement: *CAD-4 Diffractometer Control Software*. Data reduction: *X-RED* (Stoe & Cie, 1996). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990).

Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Software used to prepare material for publication: *SHELXL93*.

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Potassium β''-aluminogallate

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Abstract

The single-crystal structure of a non-stoichiometric potassium β''-aluminogallate, $K_{1.67}Mg_{0.67}Al_{8.58}Ga_{1.75}O_{17}$, has been determined by X-ray diffraction. The Ga atoms were found to occupy predominantly a tetrahedral $6c$ site (space group $R\bar{3}m$) in the middle of a spinel block of aluminium oxide with a site occupation of 51.6%. All the charge-stabilizing Mg^{2+} ions are found in the same site. Ga atoms are also found with a site occupation of 12.7% in the other tetrahedral $6c$ site, a site occupation of 7.6% in an octahedral $18h$ site and a site occupation of 0.9% in the second octahedral $3a$ site. The K$^+$ ions lie distributed along edge-linked hexagonal pathways with