

Fig. 4 shows the DTA curve recorded between 240 and 130 K. A small endothermic peak occurs at 168 (2) K. The peak is completely reversible with a slight hysteresis of about 5 K. Because the base line is not completely linear an exact value for the change in free enthalpy and consequently in the entropy should not be estimated. The peak in the DTA curve lies in the same temperature range as observed in the magnetic susceptibility curve (Fig. 3).

The structure of the title compound shows an unusual connection scheme with edge- and face-sharing octahedra. This leads to distorted $V(S,Se)_6$ octahedra with short metal-metal bonds in the structure. The partial itinerant character of this compound is supported by the magnetic measurements. The discontinuity in the magnetic-susceptibility curve and the endothermic peak in the DTA curve are a clear indication for a phase transition at around 170 K. Further investigations are in progress to clarify the nature of this phase transition.

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Structure of Kamiokite

BY Y. KANAZAWA AND A. SASAKI

Geological Survey of Japan, Tsukuba, Ibaraki 305, Japan

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Abstract. $Fe_2Mo_3O_8$, $M_r = 527.51$, hexagonal, $P6_3mc$, $a = 5.781$ (1), $c = 10.060$ (1) Å, $V = 291.2$ (1) Å³, $Z = 2$, $D_m = 5.96$, $D_x = 6.02$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu(Mo K\alpha) = 11.14$ mm⁻¹, $F(000) = 484$, $T = 298$ K, $R = 0.027$ for 656 independent reflections. In the structure, the layer composed of MoO_6 octahedra alternates with the layer composed of FeO_6 octahedra and FeO_4 tetrahedra along c . These polyhedra are linked together by edges and corners to form a three-dimensional network. The very short Mo–Mo bond length of 2.533 (1) Å confirms the presence of triangular clusters of bonded Mo atoms.

Introduction. Kamiokite, $Fe_2Mo_3O_8$, was first described as a new mineral by Sasaki, Yui & Yamaguchi (1975) from the Kamioka mine, Gifu Prefecture, central Japan. It was also reported from the Mohawk and Ahmeek mines, Michigan (Picot & Johan, 1977). We here

present the result of a crystal structure analysis of the type mineral specimen from Kamioka. The chemical composition of the specimen was reported as $(Fe_{2.01}Mn_{0.03})_{2.04}Mo_{2.98}O_8$ (Sasaki *et al.*, 1975), which was very close to the ideal composition.

The mineral belongs to the ternary oxide group with the formula $M_2^I Mo_3^IV O_8$ (where $M = Mg, Mn, Fe, Co, Ni, Zn$ and Cd). The members of this group were prepared and examined systematically by McCarroll, Katz & Ward (1957) who reported that the compounds were isostructural because of the similar characteristics of their X-ray powder diffraction patterns; they presented the results of structure determinations on $Zn_2Mo_3O_8$ and $Mg_2Mo_3O_8$. Later a refinement of the structure was accomplished by Ansell & Katz (1966) on $Zn_2Mo_3O_8$, confirming the previously reported structural features. The result is used as the basis for the present work on $Fe_2Mo_3O_8$ (kamiokite).

Experimental. D_m by suspension in CCl_4 . Cube-shaped crystal $0.070 \times 0.070 \times 0.062$ mm. Rigaku AFC-5 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Lattice parameters from 25 reflections with $60^\circ < 2\theta < 80^\circ$. Intensities measured up to $2\theta = 103^\circ$; h 0–11, k 0–11, l 0–22, ω – 2θ scans. Two standard reflections (220, 008) every 50 reflections, variation less than 1% about mean. 668 independent reflections, 656 with $|F_o| > 3\sigma(|F_o|)$. Lorentz and polarization but no absorption or extinction correction. Atomic coordinates, anisotropic thermal parameters and a scale factor refined by full-matrix least squares on F using the atomic parameters of $\text{Zn}_2\text{Mo}_3\text{O}_8$ (McCarroll, Katz & Ward, 1957) as the initial ones; $R = 0.027$, $wR = 0.037$, $S = 2.62$; unit weights; $(\Delta/\sigma)_{\text{max}} = 0.01$; final $\Delta\rho \leq 12.51 \text{ e } \text{Å}^{-3}$; atomic scattering factors of Fe^{2+} and Mo^{4+} [$(\text{Mo}^{3+} + \text{Mo}^{5+})/2$] including f' and f'' values from *International Tables for X-ray Crystallography* (1974) and of O^{2-} from Tokonami (1965); programs for least squares and for bond distances and angles by Finger & Prince (1975); *UNICS* for Fourier synthesis (Sakurai, 1967).

Table 1. Positional parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

Wyckoff notation	x	y	z	$B_{\text{eq}}(\text{Å}^2)$
Fe(1)	$\frac{1}{2}(b)$	$\frac{1}{2}$	0.9504 (2)	0.54 (1)
Fe(2)	$\frac{1}{2}(b)$	$\frac{1}{2}$	0.5120 (2)	0.44 (1)
Mo	$6(c)$	0.14603 (4)	0.29206 (4)	0.253 (1)
O(1)	$2(a)$	0	0	0.3923 (9)
O(2)	$2(b)$	$\frac{1}{2}$	$\frac{2}{3}$	0.1486 (9)
O(3)	$6(c)$	0.4872 (5)	0.9744 (5)	0.3645 (5)
O(4)	$6(c)$	0.1665 (5)	0.3330 (5)	0.6352 (5)

Table 2. Selected bond distances (Å) and angles ($^\circ$)

Fe tetrahedron					
Fe(1)–O(2 ⁱ)	1.994 (9)	O(2 ⁱ)	–Fe(1)–	O(3 ⁱⁱ)	115.7 (1)
O(3 ⁱⁱ)	1.993 (3) (x3)	O(3 ⁱⁱ)	–Fe(1)–	O(3 ^{vii})	102.6 (2)
Mean:	1.993				
Fe octahedron					
Fe(2)–O(3)	2.139 (4) (x3)	O(3)	–Fe(2)–	O(3 ⁱⁱ)	77.2 (2)
O(4)	2.080 (4) (x3)	O(3)	–Fe(2)–	O(4)	172.7 (2)
		O(3)	–Fe(2)–	O(4 ⁱⁱ)	97.1 (2)
Mean:	2.110	O(4)	–Fe(2)–	O(4 ⁱⁱⁱ)	88.2 (2)
Mo octahedron					
Mo–O(1)	2.047 (6)	O(1)	–Mo–	O(2)	164.1 (3)
O(2)	2.135 (4)	O(1)	–Mo–	O(3 ⁱⁱⁱ)	89.5 (2)
O(3 ⁱⁱⁱ)	2.081 (4) (x2)	O(1)	–Mo–	O(4 ^{vi})	100.6 (2)
O(4 ^{vi})	1.953 (4) (x2)	O(2)	–Mo–	O(3 ⁱⁱⁱ)	78.3 (2)
Mean:	2.042	O(2)	–Mo–	O(4 ^{vi})	90.0 (2)
		O(2)	–Mo–	O(3 ^{iv})	79.8 (2)
		O(3 ⁱⁱⁱ)	–Mo–	O(4 ^{vi})	91.4 (1)
		O(3 ⁱⁱⁱ)	–Mo–	O(4 ^{viii})	166.6 (1)
		O(3 ⁱⁱⁱ)	–Mo–	O(4 ^{vii})	95.3 (2)
Mo–Mo ⁱⁱ	2.5326 (5) (x2)				
Mo ^{vi}	3.2486 (5) (x2)				

Symmetry code: none x, y, z ; (i) $x, y, z + 1$; (ii) $-y, -x, z$; (iii) $1 - y, 1 - x, z$; (iv) $x, x - y + 1, z$; (v) $1 - x, 2 - y, z + \frac{1}{2}$; (vi) $y, x, z - \frac{1}{2}$; (vii) $y - 1, x, z + \frac{1}{2}$; (viii) $-x, y - x, z - \frac{1}{2}$.

Discussion. The final positional parameters are presented in Table 1* and atomic distances and angles in Table 2. The structure is shown in Fig. 1. The crystal structure (with space group $P6_3mc$) is isomorphous with that of $\text{Zn}_2\text{Mo}_3\text{O}_8$, i.e. the structure consists of a distorted double-hexagonal closest packing of O atoms (abc_b) in which the O layers are held together by alternate layers of Fe and Mo atoms. Half of the Fe atoms are in tetrahedral coordination with O atoms while the other half are in octahedral coordination. On the other hand, the Mo atoms are in octahedral coordination with O atoms. MoO_6 octahedra are linked together by edges to form the Mo layer, to which FeO_6 octahedra are connected by sharing both edges and corners and FeO_4 tetrahedra by corners.

A remarkable feature of the structure is the strong Mo–Mo bonding with a very short distance of 2.533 Å, which is close to the value of 2.524 (2) Å found in $\text{Zn}_2\text{Mo}_3\text{O}_8$ by Ansell & Katz (1966). These short distances are rather conspicuous among common

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42479 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

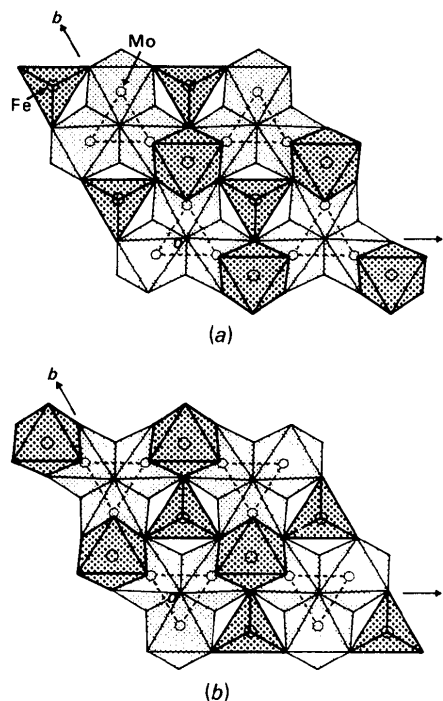


Fig. 1. Projection of the crystal structure along c with the MoO_6 , FeO_4 and FeO_6 polyhedra. The Mo–Mo bonding is shown by dotted lines. (a) Projection from $z = \sim 0.15$ to ~ 0.65 . (b) Projection from $z = \sim 0.65$ to ~ 1.15 .

molybdenum oxides, while even stronger Mo—Mo bondings such as the triple bond (Chisholm, Cotton, Extine & Murillo, 1978) and the quadruple bond (Cotton, Extine & Gage, 1978) have been known in some non-oxide compounds. The Mo—Mo bonding concerned forms the triangular atom groups of Mo_3O_{13} in the MoO_6 layer (Fig. 1). Such a group was termed 'metal-atom cluster' and the strong metal-to-metal bonding was already established for Mo_3O_{13} using the LCAO—MO calculation by Cotton (1964). The short Mo—Mo bond may have caused the variation in the Mo—O distance which ranges from 1.953 to 2.135 Å, giving distorted MoO_6 octahedra. On the other hand, Fe—O distances in both FeO_4 and FeO_6 polyhedra are found to be normal (Shannon & Prewitt, 1969).

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Structure of Barium Dipotassium Hexanitrocobaltate(II): a Redetermination

BY JAMES K. BEATTIE, TREVOR W. HAMBLEY AND CHRISTOPHER J. MOORE

Department of Inorganic Chemistry, University of Sydney, Sydney 2006, Australia

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Abstract. $\text{BaK}_2[\text{Co}(\text{NO}_2)_6]$, $M_r = 550.5$, cubic, $Fm\bar{3}$, $a = 10.653(2)$ Å, $V = 1209.0$ Å³, $Z = 4$, $D_x = 3.024$ g cm⁻³, $\text{Mo } K\alpha$, $\lambda = 0.71069$ Å, $\mu = 53.45$ cm⁻¹, $F(000) = 1036$, $T = 294$ K, final $R = 0.027$ for 323 reflections. The $[\text{Co}(\text{NO}_2)_6]^{4-}$ anion has $m\bar{3}$ (T_h) symmetry. The Co—N distance is 2.010(3) Å, which is only 0.06 Å longer than in an analogous Co^{III} complex. The thermal ellipsoid of the N atom reveals no anisotropy, in contrast with other structures containing the same complex anion.

Introduction. Low-spin octahedral complexes of d^7 ions are expected to be distorted by a Jahn–Teller effect. However, compounds of the type $M^{\text{II}}M^{\text{I}}_2[\text{Co}(\text{NO}_2)_6]$ are cubic with all Co—N distances equal (Lenhert & Joesten, 1980; Bertrand & Carpenter, 1966). It is possible that the octahedral symmetry is the result of a dynamic rather than static Jahn–Teller effect.

The structure of $\text{BaK}_2[\text{Co}(\text{NO}_2)_6]$ has been determined twice previously: at room temperature where octahedral symmetry about Co was observed (Bertrand & Carpenter, 1966) and at 233 K where three different Co—N distances were observed (Bertrand, Carpenter & Kalyanaraman, 1971). In both cases the structures

were determined from film data and hence were of limited precision. Recent, precise determinations of the structures of $\text{PbK}_2[\text{Co}(\text{NO}_2)_6]$ and $\text{PbRb}_2[\text{Co}(\text{NO}_2)_6]$ (Lenhert & Joesten, 1980) have revealed anisotropic thermal parameters suggestive of a dynamic Jahn–Teller effect. In order to establish whether such an effect is also evident in the title compound, and to obtain more precise bond lengths for comparison with the aforementioned compounds, we have redetermined its structure using counter-measured data.

Experimental. Data collected using Enraf–Nonius CAD-4 automatic diffractometer, graphite-monochromated $\text{Mo } K\alpha$ radiation; 18 independent reflections with $20^\circ \leq 2\theta \leq 65^\circ$ used for least-squares determination of cell constant. Intensities of three reflections monitored, less than 1% decomposition. Full-matrix least-squares refinement based on F values, starting from previously published coordinates (Bertrand & Carpenter, 1966), converged with all shifts less than 0.001σ . Max. excursions in final difference map 0.8 and -1.1 e Å⁻³. All calculations performed with *SHELX76* (Sheldrick, 1976). Scattering factors and anomalous-dispersion terms taken from *International*