X-ray Rietveld Structure Determination of $Cs_2CuSi_5O_{12}$, a Pollucite Analogue

BY A. R. HEINRICH* AND CH. BAERLOCHER

Institut für Kristallographie, ETH Zentrum, CH-8092 Zürich, Switzerland

Abstract. $M_r = 661.8$, tetragonal, $P4_12_12$, $a = b = 13.5776$ (1), $c = 13.6189$ (2) Å, $V = 2510.66$ (8) Å^3, $Z = 8$, $F(000) = 2440$, room temperature, final $R_{wp} = 0.145$, Cu $K\alpha_1$, $\lambda = 1.54056$ Å, quartz monochromator. In the white title compound Cu^{II} and Si^{IV} replace Al^{III} in the tetrahedral sites of the analcime-like (Si,Al–O) framework of pollucite.

Introduction. In recent years the replacement of Si by transition-metal cations in zeolitic frameworks has been of interest because of its potential to enhance their catalytic property. ZSM-5 was synthetized containing cobalt (Rossin, Saldarriaga & Davis, 1987) and iron(III) (Calis, Frenken, DeBoer, Swolfs & Hefni, 1987; Szostak, Nair & Thomas, 1987) on framework sites. Fe^{III} was also reported in the framework of pentosil-group zeolites (Ratnasamy, Borade, Sivasanker & Shiralkar, 1985), and in erionite and mordenite (Kljueva, Nguyen Duc Tien & Ione, 1985). In all these examples a small fraction of the transition metal present in the educt was incorporated in the zeolite framework, whereas the bulk was bound to O atoms within its pores or remained as separate oxide phases on the surface of the zeolite.

Pollucite ($CsAlSi_2O_6$) is a zeolite-like aluminosilicate with the same framework as analcime. Kopp, Harris, Clark & Yakel (1963) first hydrothermally synthetized a pink Fe^{III} analogue of pollucite with a random distribution of Fe and Si. Kume & Koizumi (1965) observed a linear increase in the lattice constants and a deepening of the reddish brown colour with increasing iron content of an Fe–Al solid solution series. Bayer (1973) prepared pollucites with the composition $Cs_2MSi_5O_{12}$ (M = Be, Mg, Co, Ni, Cu, Zn) by solid-state reaction at 1073–1373 K. The copper-containing sample was bright blue and had a cubic *I*-centred lattice.

Experimental. The title compound was synthetized in two steps. First a mixture of analytically pure Cs_2CO_3, CuO and $5SiO_2$ was pressed into a pellet and tempered at 873 K for 136 h. This yielded an X-ray pure cubic pollucite with diffuse powder lines.

Then, the sample was welded in a gold capsule of 2.5 mm inner diameter and 30 mm length, which was kept in a hydrothermal (cold seal) pressure vessel at 10^8 Pa and 723 K for two weeks. To prevent formation of the double sheet silicate $Cs_2Cu_2Si_8O_{19}$ (Heinrich & Gramlich, 1982), 1*M* CsOH solution was used instead of water. Solid:fluid ratio at synthesis conditions was approximately 2:1 by volume. Since the crystals still showed diffuse powder lines, the same hydrothermal procedure was repeated with addition of pure water. The resulting sample consisted of almost spherical crystals, up to 1.5 μm in diameter, with partially developed crystal faces (Fig. 1). Electron microprobe analysis shows an average composition of $0.94Cs_2O : 0.97CuO : 5.04SiO_2$. Oxide concentrations varied by up to 5%, but Si + Cu summed to 6.00 ± 0.02 atoms per formula unit, and the measured oxides total 99.99 wt%. Standards used were the double sheet silicate $Cs_2Cu_2Si_8O_{19}$, Cu_2O and the feldspar $KAlSi_3O_8$. There was some

Fig. 1. Scanning electron micrograph of the pollucite analogue $Cs_2CuSi_5O_{12}$.

* Present address: Geology Department, Australian National University, GPO Box 4, Canberra, ACT2601, Australia.

evidence for Cs mobilization during electron irradiation. The lattice constants are virtually identical to those of pollucite $Cs_2Al_2Si_4O_{12}$, prepared by sintering at 873 K for 136 h and 1373 K for 36 h, and do not vary in the solid solution series $Cs_2Al_{2(1-x)}Cu_x$-$Si_{4+x}O_{12}$. The colour of the intermediate Al + Cu containing samples is blue, whereas the pure end members ($x = 0$ or 1) are white. The absence of colour could be an indication that all the Cu are tetrahedrally coordinated in the Cu end member. This is in agreement with Szostak *et al.* (1987), who found that isomorphic replacement of tetrahedrally coordinated Al in ZSM5 by Fe^{III} resulted in a colourless (white) product.

The powder pattern of Cu-substituted pollucite shows superstructure reflections of low intensity, which are incompatible with the extinction rules of $Ia3d$, the space group of pollucite (Beger, 1969). This, and slight splitting of the cubically indexed lines, indicated a non-cubic symmetry. The pattern could finally be indexed with a primitive tetragonal lattice. The primitive superstructure reflections also appear gradually in samples tempered in air at 1173 K for increasing periods of 8 to 16 h. However, the tetragonal splitting is only expressed as a line broadening in these samples, whereas in the hydrothermal sample it is evident as two partly overlapping peaks. No superstructure lines could be seen in the powder patterns of Be-, Mg-, Ni- or Zn-substituted pollucites, which were also prepared by sintering.

A powder diffraction pattern from the hydrothermal sample, loosely packed into a flat plastic holder (15 × 30 mm), was recorded on a PAD-1 diffractometer (Baerlocher & Moeck, 1975) at room temperature and interpreted using *The X-ray Rietveld System* (Baerlocher, 1982). For the different divergence slit settings the pattern was scaled according to the integrated intensity of peak (400 at $2\theta = 26\cdot23°$), which was remeasured periodically throughout the experiment and was found to be stable. Values for the low background were measured in regions between well separated peaks. Linear interpolation of these values yielded the background correction for all data points. The lattice constants were refined with $c > a$ (*cf. Abstract*), because the reflections at higher 2θ values of the split 400 and 800 reflections were more intensive than those at lower 2θ values, reflecting the difference in multiplicity of $h00 + 0k0$ and $00l$ reflections. Then the 2θ correction was calculated and applied to the experimental profile. To determine the experimental peak shape function (Hepp & Baerlocher, 1988), the peak 221 at $2\theta = 15\cdot97°$ was chosen. Peaks at higher 2θ values were unsuitable because they show shoulders or broadening due to the tetragonal splitting. Using the peak shape function, the entire profile was then analysed

Table 1. *Crystallographic data specific to the structure refinement*

Pattern 2θ range (2θ)	15·5–93·6°
Step-scan increment (2θ)	0·02°
Standard peak for peak shape function	221 at $2\theta = 15\cdot97°$
Number of steps	3684
Number of contributing reflections	685
Absorption correction	None
Extinction correction	None
Preferred orientation	None detected
Number of geometric restrictions	72
Number of structural parameters	99
Number of profile parameters	8
R_{wp} (beginning, ideal pollucite model)	0·387
R_{wp} (end)	0·145
R_F	0·116
R_{exp}	0·119
R_I	0·15
Largest correlation element (unblocked matrix)	0·75
Largest correlation element (blocked matrix)	0·5

Restraints (e.s.d.'s in brackets)

Si—O···Si	1·61	(0·01)
Si—O···Cu	1·58	(0·01)
Cu—O···Si	1·93	(0·02)
O—Si—O	109·5	(5·0)
O—Cu—O	109·5	(10·0)

for the dependence of peak width and peak asymmetry on 2θ. Atomic scattering factors for neutral atoms were used (*International Tables for X-ray Crystallography*, 1974, Vol. IV). Details specific to the structure refinement are included in Table 1. Further details are given by Heinrich (1983).

In order to determine the phases of the primitive superstructure reflections, a trial and error attempt was made to locate the Cs atom within an analcime framework, in which part of the Si were substituted by Cu.

In $Ia3d$, the Cs atoms are located on the crosspoints of the three- and twofold axes and are therefore completely restricted. The primitive subgroup $P4_132$ allows half of the Cs atoms to be shifted along the threefold axis. This shift produces reflections at lower 2θ angles than the observed primitive superstructure reflections. Therefore the symmetry was reduced further to primitive tetragonal. The four primitive tetragonal subgroups to $Ia3d$ with the highest symmetry compatible with the measured pattern are $P\bar{4}b2$, $P\bar{4}c2$, $P4_122$ and $P4_12_12$, in all of which half of the Cs atoms are in a general position. With a shift of these generally positioned Cs atoms along c the appearance of the observed superstructure lines could be qualitatively explained.

The fact that superstructure reflections occur at all suggests an ordered distribution of copper. If one assumes that the 8 Cu and 40 Si atoms share the 48 tetrahedral sites in the unit cell, then there are six possibilities in each of the four primitive tetragonal space groups. Some of these can be excluded with symmetry and crystal chemical considerations:

(*a*) The 48 symmetrically equivalent tetrahedral sites in $Ia3d$ split into five general and two special

positions during symmetry reduction. The latter two, and one general position, are derived from the 16(*f*) position in $I4_1/acd$, a tetragonal subgroup to $Ia3d$, in which analcime was refined (Mazzi & Galli, 1978). Placing copper on these positions would cause an *I*-centred copper distribution, which would not give any reason for primitive superstructure reflections.

(*b*) Of each enantiomorphic pair, only one possibility needs to be considered.

(*c*) It is unlikely that two Cu atoms are in the tetrahedra next to each other, and models which would concentrate the eight Cu atoms on the four corners of two four-membered rings in $P\overline{4}b2$ and $P\overline{4}c2$ were excluded.

(*d*) The shift of Cs along **c** suggests that Cs has a different surrounding in the positive and negative *c*-axis direction. Therefore, Cu atoms should be located in the tetrahedra above or below Cs atoms.

After this procedure three possibilities remained for the X-ray refinement, one each in $P4_12_12$, $P4_122$ and $P\overline{4}c2$, for which starting models were calculated using the distance and angle least-squares program *DLS* (Baerlocher, Hepp & Meier, 1977). The high symmetry of the original Al–pollucite framework was reduced by introducing Cs—O bonds with small weights for the Cs atoms which were shifted along **c**. In the following Rietveld refinement those Cs—O bonds were dropped, but restraints (distances and angles) were used for the framework atoms. As the structure refinement progressed the weight of these restraints was decreased until their contribution to

the least-squares function was less than 10% of the contribution of the intensity data. All attempts to refine the structure in $P\overline{4}c2$ failed, because some important superstructure reflections such as 411 and 330 could not be explained. Refinement of the data with the $P4_122$ model did not converge well and was terminated. By contrast, the refinement of the $P4_12_12$ model converged rapidly to a final $R_{wp} = 0.145$. Since the positional parameters of the Cu and Si atoms were partially correlated with the positional parameters of the coordinated O atoms, cations and anions were refined in two separate blocks. The temperature factors of the O atoms were refined with damping factors to avoid excessive fluctuations. In the last refinement cycle the ratio of the parameter shifts to their standard deviations was less than 1·5. A difference electron density map did not show any significant peaks. The measured and calculated X-ray patterns as well as their difference is shown in Fig. 2.* The atomic parameters are listed in Table 2 and selected interatomic distances and angles in Table 3.

Discussion. The framework topology is that of the type ANA (Meier & Olson, 1987). The eight Cu

---

* The magnetic tape containing the numerical data reported in Fig. 2 has unfortunately been lost. However, a list of the raw, scaled intensity data has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53694 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
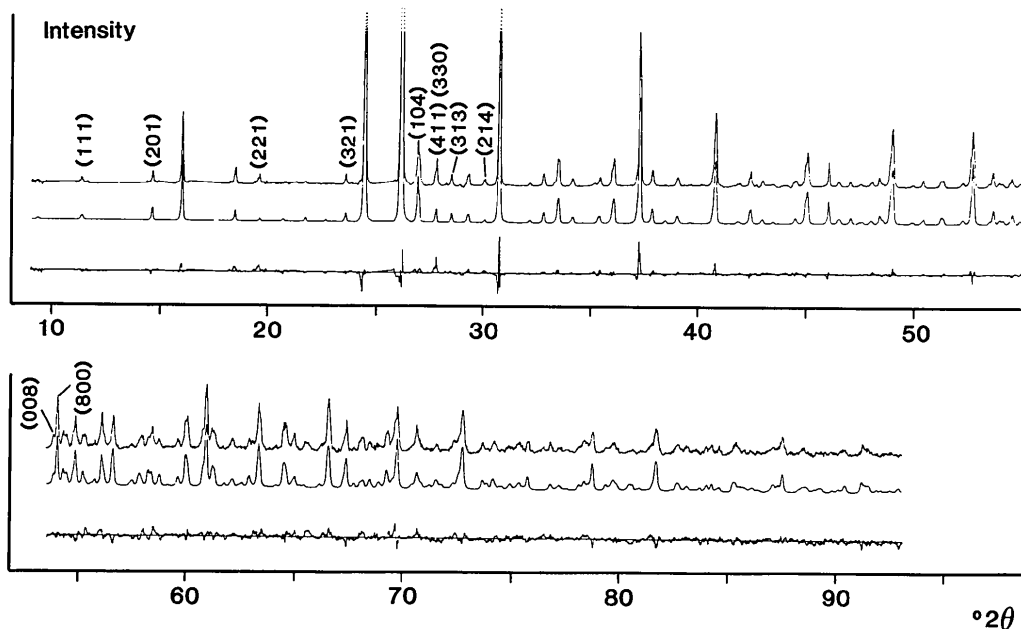

Fig. 2. Measured (upper) and calculated (centre) X-ray patterns, and their difference (bottom profile). Note the splitting of 800 and primitive superstructure reflections such as 111, 201, 221, 320, 411, 330, 104, 313 and 214, which is inconsistent with $Ia3d$, the space group of pollucite.

Table 2. *Atomic coordinates, isotropic temperature factors B and population parameters PP (the population parameters of the O atoms were not refined), with e.s.d.'s in parentheses*

		x	y	z	$B(Å^2)$	PP
Cs(1)	8(*b*)1	0.8810 (4)	0.6322 (5)	0.5235 (2)	1.62 (6)	0.991 (1)
Cs(2)	4(*a*)2	0.8853 (7)	0.8853 (7)	0	7.6 (2)	0.996 (1)
Cs(3)	4(*a*)2	0.6183 (5)	0.6183 (5)	0	2.0 (1)	1.001 (2)
Cu	8(*b*)1	0.6070 (8)	0.1695 (7)	0.4498 (6)	3.2 (3)	0.983 (2)
Si(1)	8(*b*)1	0.8735 (8)	0.3234 (8)	0.4794 (7)	2.8 (8)	0.986 (4)
Si(2)	8(*b*)1	0.3946 (8)	0.0803 (8)	0.4779 (8)	7.4 (9)	1.079 (5)
Si(3)	8(*b*)1	0.8292 (8)	0.1253 (8)	0.5391 (8)	2.1 (9)	0.878 (5)
Si(4)	8(*b*)1	0.6561 (8)	0.3818 (8)	0.5362 (8)	5 (1)	0.969 (5)
Si(5)	4(*a*)2	0.0896 (7)	0.0896 (7)	0	3 (2)	0.918 (7)
Si(6)	4(*a*)2	0.3838 (7)	0.3838 (7)	0	4 (1)	0.997 (6)
O(1)	8(*b*)1	0.589 (2)	0.311 (1)	0.466 (2)	2 (2)	
O(2)	8(*b*)1	0.713 (1)	0.108 (2)	0.526 (2)	7 (3)	
O(3)	8(*b*)1	0.774 (1)	0.358 (2)	0.533 (2)	8 (2)	
O(4)	8(*b*)1	0.872 (2)	0.206 (1)	0.468 (2)	4 (2)	
O(5)	8(*b*)1	0.510 (1)	0.080 (2)	0.506 (2)	4 (2)	
O(6)	8(*b*)1	0.630 (2)	0.165 (2)	0.312 (1)	2 (1)	
O(7)	8(*b*)1	0.968 (1)	0.360 (2)	0.541 (2)	3 (2)	
O(8)	8(*b*)1	0.877 (2)	0.356 (2)	0.366 (1)	2 (1)	
O(9)	8(*b*)1	0.891 (1)	0.029 (1)	0.507 (2)	1 (2)	
O(10)	8(*b*)1	0.838 (2)	0.163 (2)	0.653 (1)	1 (2)	
O(11)	8(*b*)1	0.635 (2)	0.361 (2)	0.653 (1)	6 (2)	
O(12)	8(*b*)1	0.636 (2)	0.496 (1)	0.501 (2)	7 (2)	

Table 3. *Selected distances and angles: e.s.d.'s for distances and angles are approximately 0.05 Å and 3°, respectively*

Cs(1)—O(2)	3.03		Si(1)—O(3)	1.61
—O(10)	3.17		—O(4)	1.60
—O(5)	3.20		—O(7)	1.61
—O(11)	3.27		—O(8)	1.60
—O(2)	3.34		Average	1.61
—O(10)	3.41			
—O(5)	3.42		Si(2)—O(5)	1.62
—O(7)	3.45		—O(6)	1.56
—O(3)	3.52		—O(7)	1.62
—O(11)	3.58		—O(8)	1.57
			Average	1.59
Cs(2)—O(6)	3.11		Si(3)—O(2)	1.61
—O(1)	3.12		—O(4)	1.58
—O(9)	3.26		—O(9)	1.61
—O(4)	3.54		—O(10)	1.63
Cs(3)—O(1)	3.02		Average	1.61
—O(4)	3.20		Si(4)—O(1)	1.63
—O(6)	3.58		—O(3)	1.63
—O(8)	3.60		—O(11)	1.64
Cu—O(1)	1.95		—O(12)	1.64
—O(2)	1.95		Average	1.63
—O(5)	1.94			
			Si(5)—O(9)	
—O(6)	1.90		—O(11)	1.60
Average	1.93		Average	1.61
			Si(6)—O(10)	1.61
			—O(12)	1.65
			Average	1.62

O(3)—Si(1)—O(4)	109		O(9)—Si(5)—O(9)	109
O(3)—Si(1)—O(7)	110		O(9)—Si(5)—O(11)	107
O(3)—Si(1)—O(8)	112		O(11)—Si(5)—O(9)	111
O(4)—Si(1)—O(7)	111		O(11)—Si(5)—O(11)	111
O(4)—Si(1)—O(8)	100		O(10)—Si(6)—O(10)	112
O(7)—Si(1)—O(8)	113		O(10)—Si(6)—O(12)	109
O(5)—Si(2)—O(6)	109		O(12)—Si(6)—O(10)	109
O(5)—Si(2)—O(7)	109		O(12)—Si(6)—O(12)	109
O(5)—Si(2)—O(8)	110		O(1)—Cu—O(2)	117
O(6)—Si(2)—O(7)	112		O(1)—Cu—O(5)	119
O(6)—Si(2)—O(8)	107		O(1)—Cu—O(6)	99
O(7)—Si(2)—O(8)	110		O(2)—Cu—O(5)	91
O(2)—Si(3)—O(4)	113		O(2)—Cu—O(6)	113
O(2)—Si(3)—O(9)	111		O(5)—Cu—O(6)	119
O(2)—Si(3)—O(10)	103		Si(1)—O(3)—Si(4)	153
O(4)—Si(3)—O(9)	102		Si(1)—O(4)—Si(3)	130
O(4)—Si(3)—O(10)	110		Si(1)—O(7)—Si(2)	139
O(9)—Si(3)—O(10)	118		Si(1)—O(8)—Si(2)	161
O(1)—Si(4)—O(3)	114		Si(3)—O(9)—Si(5)	154
O(1)—Si(4)—O(11)	112		Si(3)—O(10)—Si(6)	134
O(1)—Si(4)—O(12)	107		Si(4)—O(11)—Si(5)	154
O(3)—Si(4)—O(11)	100		Si(4)—O(12)—Si(6)	164
O(3)—Si(4)—O(12)	110		Cu—O(1)—Si(4)	125
O(11)—Si(4)—O(12)	114		Cu—O(2)—Si(3)	136
			Cu—O(5)—Si(2)	124
			Cu—O(6)—Si(2)	132

atoms per unit cell, which were found to occupy one-sixth of the tetrahedral framework sites, cause a strong distortion (see, for example, four-membered rings in Fig. 3). The coordination polyhedron of Cu is an elongated tetrahedron, with two angles opposite each other being clearly smaller (approx. 95°) than the four remaining ones (approx. 117°), and with an average Cu—O distance of 1.93 Å. Such a copper coordination has, to our knowledge, not been reported before. It is clearly not caused by the choice of the starting parameters, because it was refined from an almost regular tetrahedron with a Cu—O distance of 1.92 Å. The Si—O distances and angles are within the reasonable range of 1.56–1.65 Å and 100–114°, respectively. As in ordinary pollucite (Beger, 1969), the Cs atoms occupy the large cavities. For O atoms connecting a Cu- and an Si-containing tetrahedron, the Cs—O distances are relatively short (3.02 Å min.) presumably to compensate for the underbonding of the O atoms. The Cs—O distances to O atoms connecting two Si tetrahedra are within the range of Cs—O distances found in other caesium-containing zeolites (McCusker & Baerlocher, 1983; Annehed & Faelth, 1984; Schlenker, Pluth & Smith, 1978).

The Cu and Si atoms are at average distances of 3.20 and 3.08 Å, respectively, to the Si atom of the adjacent tetrahedron. The average of these two values is identical to the mean Al⋯Si distance of 3.14 Å in aluminosilicates calculated from the average Si—O—Al angle of 130° and the average Si—O and Al—O distances of 1.62 and 1.74 Å, respectively (Gibbs, 1982). This might explain the absence of any variation in the lattice constant within the solid

solution series $Cs_2Al_{2(1-x)}Cu_xSi_{4+x}O_{12}$, in which the two Al atoms are replaced isomorphically by Cu and Si atoms.

Although there is no evidence in the powder pattern, the symmetry of the compound could be still lower, for example, orthorhombic like wairakite (Takeuchi, Mazzi, Haga & Galli, 1979). Also, a Cu-atom distribution consistent with the $P4_122$ model cannot be excluded with certainty, despite the
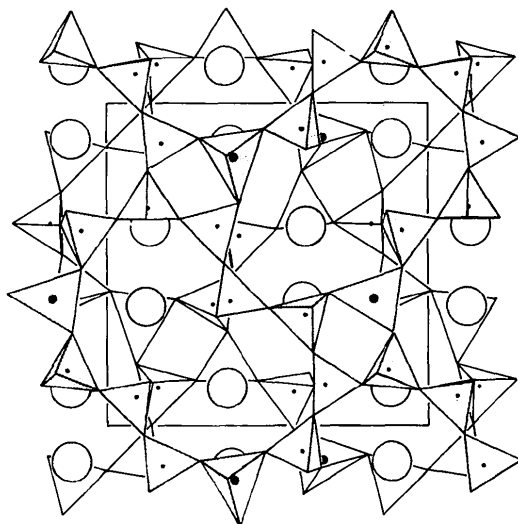
Fig. 3. Projection of the lower half of the unit cell of $Cs_2CuSi_5O_{12}$ on (001). Cs is represented by the large open and filled circles. Si and Cu are shown as small and large dots, respectively, inside the tetrahedra.

slow convergence during attempted refinement. However, population parameters in the refined $P4_12_12$ model close to their ideal values (Table 2) suggest that the $P4_12_12$ distribution is correct. Independent of this possible ambiguity, the structure refinement clearly shows that copper is incorporated in the Si—O framework of the zeolite-like pollucite structure.

References

ANNEHED, H. & FAELTH, L. (1984). Z. Kristallogr. 166, 301–306.
BAERLOCHER, CH. (1982). The X-ray Rietveld System XRS82. Institut für Kristallographie und Petrographie, ETH, Zürich, Switzerland.
BAERLOCHER, CH., HEPP, A. & MEIER, W. M. (1977). DLS76, a Program for the Simulation of Crystal Structures by Geometric Refinement. Institut für Kristallographie und Petrographie, ETH, Zürich, Switzerland.
BAERLOCHER, CH. & MOECK, H. (1975). Acta Cryst. A31, S237.
BAYER, G. (1973). Naturwissenschaften, 60, 102–103.
BEGER, R. M. (1969). Z. Kristallogr. 129, 280–302.
CALIS, G., FRENKEN, P., DEBOER, E., SWOLFS, A. & HEFNI, M. A. (1987). Zeolites, 7, 319–326.
GIBBS, G. V. (1982). Am. Mineral. 67, 421–450.
HEINRICH, A. (1983). PhD dissertation. Number 7303. ETH, Zurich, Switzerland.
HEINRICH, A. & GRAMLICH, V. (1982). Naturwissenschaften, 69, 142–143.
HEPP, A. & BAERLOCHER, CH. (1988). Austr. J. Phys. 41, 229–236.
KLJUEVA, N. V., NGUYEN DUC TIEN & IONE, K. G. (1985). Acta Phys. Chem. 31, 525–534.
KOPP, O. C., HARRIS, L. A., CLARK, G. W. & YAKEL, H. L. (1963). Am. Mineral. 48, 100–110.
KUME, S. & KOIZUMI, M. (1965). Am. Mineral. 50, 587–592.
MCCUSKER, L. B. & BAERLOCHER, CH. (1983). Proceedings of the Sixth International Zeolite Conference, edited by D. OLSON & A. BISIO, pp. 812–822. Guildford: Butterworth.
MAZZI, F. & GALLI, E. (1978). Am. Mineral. 63, 448–460.
MEIER, W. M. & OLSON, D. H. (1987). Atlas of Zeolite Structure Types, 2nd revised ed., p. 24. London: Butterworth.
RATNASAMY, P., BORADE, R. B., SIVASANKER, S. & SHIRALKAR, V. P. (1985). Acta Phys. Chem. 31, 137–146.
ROSSIN, J. A., SALDARRIAGA, C. & DAVIS, M. E. (1987). Zeolites, 7, 295–300.
SCHLENKER, J. L., PLUTH, J. J. & SMITH, J. V. (1978). Mater. Res. Bull. 13, 901–905.
SZOSTAK, R., NAIR, V. & THOMAS, T. L. (1987). J. Chem. Soc. Faraday Trans. 1, 83, 483–493.
TAKEUCHI, Y., MAZZI, F., HAGA, N. & GALLI, E. (1979). Am. Mineral. 64, 993–1001.

Structure of $NdMo_8O_{14}$ Containing the New Mo_8 Cluster

BY P. GOUGEON

Université de Rennes I, Laboratoire de Chimie Minérale B, URA CNRS n° 254, Avenue du Général Leclerc, 35042 Rennes CEDEX, France

AND R. E. MCCARLEY

Ames Laboratory, USDOE, and Department of Chemistry, Iowa State University, Ames, IA 50011, USA

Abstract. Neodymium octamolybdate, $NdMo_8O_{14}$, $M_r = 1135.75$, orthorhombic, $Aba2$, $a = 9.209$ (3), $b = 10.008$ (2), $c = 11.143$ (4) Å, $V = 1026.9$ (6) Å^3, $Z = 4$, $D_x = 7.346$ g cm^{-3}, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu = 143.0$ cm^{-1}, $F(000) = 2032$, $T = 295$ K, $R = 0.021$ for 1079 observed reflections. The title compound contains the new Mo_8 cluster based on a distorted octahedron capped by two additional Mo atoms. The Mo_8 clusters are connected by bridging oxygens and arranged in layers parallel to the bc plane. The