American Mineralogist, Volume 81, pages 1277–1281, 1996

Laurelite: Its crystal structure and relationship to α-PbF_2

STEFANO MERLINO,[1] MARCO PASERO,[1] NATALE PERCHIAZZI,[1] AND ANTHONY R. KAMPF[2]

[1]Dipartimento di Scienze della Terra, Università di Pisa, via S. Maria 53, I-56126 Pisa, Italy
[2]Mineralogy Section, Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, California 90007, U.S.A.

ABSTRACT

Laurelite, $Pb_7F_{12}Cl_2$, from the Grand Reef mine, Graham County, Arizona, is hexagonal, $P\bar{6}$, with $a = 10.267(1)$ and $c = 3.9844(4)$ Å and $Z = 1$. The crystal structure was solved by direct methods and refined to $R = 0.035$ and $R_{w2} = 0.089$ for 693 measured reflections ($F_o > 9\sigma_{F_o}$).

The structure is related to that of α-PbF_2. Both are based upon ninefold-coordinated Pb as tricapped trigonal prisms (TCTPs), which share edges and faces. The two structures can be described with respect to the face-sharing linkages of their TCTPs. The structure of α-PbF_2 consists of corrugated sheets of face-sharing TCTPs that interlock by edge-sharing perpendicular to the c axis. In laurelite, the Pb2 TCTPs form three-membered face-sharing clusters about the threefold axis that are propagated into trigonal cylinders by sharing faces in the direction of the c axis. The Pb1 and Pb3 TCTPs are linked by face-sharing into a three-dimensional framework with corresponding cylindrical voids. Asymmetric coordinations about Pb1 and Pb2 are attributed to the stereoactive lone-pair effect. Although the coordinations about the anions appear to disallow substitution of OH for F, stacking defects along the c axis provide a mechanism for accommodating limited OH or H_2O for F substitution.

A new density determination yielded 7.65(5) g/cm³, in reasonable agreement with the density of 7.77 g/cm³ calculated on the basis of the empirical formula $Pb_{0.97}[F_{1.68}Cl_{0.25}(H_2O)_{0.07}]$, $Z = 7$.

INTRODUCTION

Laurelite is a hexagonal secondary lead mineral from the Grand Reef mine, Graham County, Arizona (Kampf et al. 1989). On the basis of electron microprobe data, the chemical formula of laurelite was given as $Pb(F,Cl,OH)_2$, and Kampf et al. (1989) suggested a likely structural relationship with α-PbF_2. Merlino et al. (1995) determined the structure of penfieldite, $Pb_2Cl_3(OH)$, space group $P\bar{6}$, $a = 11.393$ and $c = 4.024$ Å, and suggested a close structural relationship between laurelite and penfieldite. The present study was undertaken to determine the structure of laurelite and to clarify its relationships with α-PbF_2, penfieldite, and the other lead halide minerals.

STRUCTURE DETERMINATION

X-ray intensity data were collected on a Huber four-circle diffractometer for a crystal of laurelite measuring 0.012 × 0.018 × 0.180 mm. The operating conditions were as follows: room temperature, 45 kV, 25 mA, graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å), scan mode ω-2θ, scan width 3° (2θ), scan speed 3°/min, $2\theta_{max} = 60°$, and three standard reflections measured every one hundred reflections. The cell parameters, $a = 10.267(1)$ and $c = 3.9844(4)$ Å, were obtained by least-squares fitting of 2θ values for 21 reflections centered on the diffractometer. The 2156 measured intensities ($0 \le h \le 7$, $-14 \le k \le 12$, $-5 \le l \le 5$) were corrected for Lorentz and polarization effects and reduced to 817 unique reflections. An empirical correction for the absorption effects was made using the DIFABS program (Walker and Stuart 1983). The correction factors on F were in the range 0.863–1.158. The value of R_{int} from merging equivalents was 0.0727 and 0.0442 before and after the absorption correction, respectively.

Direct methods (SHELXS86, Sheldrick 1985) were tried in the three possible space groups $P6$, $P\bar{6}$, and $P6/m$. The best E map was in the space group $P\bar{6}$ and revealed the positions of two independent Pb atoms; however, the R index did not go below 25%. At first, we were misled by the assumption that laurelite contained 12 Pb atoms per unit cell. The key to the solution of the structure was the discovery of a third independent Pb atom on the $\bar{6}$ axis, which gave a total of 14 Pb atoms per unit cell. A Fourier synthesis clearly showed the positions of the anions, which were included in the subsequent least-squares refinement cycles as either F or Cl on the basis of the heights of the corresponding peaks in the Fourier synthesis and their bond distances. The structure was refined using aniso-

0003–004X/96/0910–1277$05.00

TABLE 1. Positional and displacement parameters for laurelite

Atom	x	y	z	U*
Pb1	0.5845(1)	0.6934(1)	½	0.0164(2)
Pb1′	0.572(5)	0.710(5)	0	0.051(9)
Pb2	0.8855(1)	0.5984(1)	0	0.0162(2)
Pb2′	0.853(2)	0.568(2)	½	0.002(4)
Pb3	0	0	½	0.0291(5)
Pb3′	0	0	0	0.04(1)
Cl1	⅓	⅔	0	0.022(2)
Cl2	⅔	⅓	½	0.022(2)
F1	0.048(2)	0.620(2)	½	0.018(3)
F2	0.609(2)	0.570(2)	0	0.024(3)
F3	0.079(2)	0.868(2)	0	0.039(5)
F4	0.834(2)	0.729(2)	½	0.021(3)

Note: The site occupancy is 95.5(4)% for all atoms except Pb1′, Pb2′, and Pb3′. For these latter atoms the site occupancy is 4.5%. U is the equivalent isotropic displacement parameter U_{eq} converted from the anisotropic ones (U_{iso} for Pb1′, Pb2′, and Pb3′).

* $U = (U_{11} + U_{22} + U_{33})/3$.

tropic displacement parameters for all atoms with the SHELXL-93 program (Sheldrick 1993) to a conventional R index of 0.048 for 693 measured reflections with $F_o > 9\sigma_{F_o}$ (0.058 for all 817 data), $R_{w2} = 0.121$ (weighted R factor on F^2, as defined by Sheldrick 1993), goodness of fit = 1.141.

Three high peaks (average height 16.8 e/Å^3) in the difference-Fourier synthesis were displaced by $c/2$ from each of the Pb atoms. These are considered to be the result of stacking defects along the c axis and to correspond to partially occupied Pb atoms, designated Pb1′, Pb2′, and Pb3′. To account for this, the occupancies of all previously refined atoms (three Pb, four F, and two Cl) were set to x and those of Pb1′, Pb2′, and Pb3′ were set to $1 - x$. The refinement converged to $R = 0.035$ (0.045 for all data), $R_{w2} = 0.089$, goodness of fit = 1.145; x refined to 95.5%. Maximum and minimum heights in the final difference-Fourier synthesis are +5.0 and −2.3 e/Å^3. Of these the two highest, 5.0 and 4.4 e/Å^3, are at distances of about 0.6 Å from Pb1 and Pb2 at the same z level, and the third highest is only +1.3 e/Å^3.

The chemical formula of laurelite indicated by the structural data is $Pb_7F_{12}Cl_2$. Table 1 includes the final fractional coordinates and equivalent isotropic displacement parameters, Table 2 the anisotropic displacement parameters, Table 3 the observed and calculated structure factors, Table 4 the selected interatomic distances, and Table 5 the bond valences.[1]

TABLE 4. Bond distances (Å) for laurelite

Pb1-(F,Cl)		Pb2-(F,Cl)		Pb3-F	
F2	2.437(9)	F3[e]	2.470(18)	F4[i]	2.503(16)
F2[a]	2.437(9)	F1[e]	2.538(10)	F4[j]	2.503(16)
F4	2.441(15)	F1[f]	2.538(10)	F4[c]	2.503(16)
F1[b]	2.468(15)	F4	2.542(9)	F3[k]	2.754(13)
F1[c]	2.723(17)	F4[g]	2.542(9)	F3[l]	2.754(13)
F3[d]	2.986(15)	F2[h]	2.606(16)	F3[m]	2.754(13)
F3[c]	2.986(15)	F2	2.711(17)	F3[n]	2.754(13)
Cl1	3.160(1)	Cl2[e]	3.211(1)	F3[b]	2.754(13)
Cl1[a]	3.160(1)	Cl2	3.211(1)	F3[o]	2.754(13)

Note: Symmetry code for equivalent positions: a = $x, y, z + 1$; b = $-y + 1, x - y + 1, z$; c = $-x + y, -x + 1, z$; d = $-x + y, -x + 1, z + 1$; e = $x + 1, y, z$; f = $x + 1, y, z - 1$; g = $x, y, z - 1$; h = $-x + y + 1, -x + 1, z$; i = $x - 1, y - 1, z$; j = $-y + 1, x - y, z$; k = $-y + 1, x - y + 1, z + 1$; l = $-x + y - 1, -x, z$; m = $x, y - 1, z$; n = $x, y - 1, z + 1$; o = $-x + y - 1, -x, z + 1$.

TABLE 5. Bond valences (vu) for laurelite

	Cl1	Cl2	F1	F2	F3	F4	$\Sigma_c v$
Pb1	$\times^2 0.18^{\times 6}$		0.31 0.15	$\times^2 0.33^{\times 2}$	$\times^2 0.08^{\times 2}$	0.33	1.97
Pb2		$\times^2 0.16^{\times 6}$	$\times^2 0.25^{\times 2}$	0.21 0.16	0.30	$\times^2 0.25^{\times 2}$	1.99
Pb3					$\times^6 0.14^{\times 2}$	$\times^3 0.28$	1.68
$\Sigma_a v$	1.08	0.96	0.96	1.03	0.74	1.11	

Note: The superscripts indicate the number of equivalent bonds for each cation (left) and each anion (right). Constants from Brese and O'Keeffe (1991).

DESCRIPTION OF THE STRUCTURE

Comparison to similar compounds

Despite having the same space group and similar compositions, laurelite and penfieldite possess quite distinct structures. In penfieldite, Pb is eightfold coordinated and its ligands form a bicapped trigonal prism (Merlino et al. 1995). In laurelite, each Pb is ninefold coordinated in the form of tricapped trigonal prisms (TCTPs). The structure of laurelite is best compared to that of α-PbF_2 (Boldrini and Loopstra 1967).

The structures of both laurelite and α-PbF_2 are based on TCTPs that share edges and faces. Projections of the two structures (Figs. 1 and 2) in the direction of their short-cell dimensions, c (3.98 Å) in laurelite and b (3.90 Å) in α-PbF_2, appear very similar. The TCTPs in both structures are oriented with their "trigonal" faces perpendicular to the aforementioned short-cell directions. The trigonal faces are shared with those of equivalent TCTPs directly above and below, forming uninterrupted tubes along the short-cell directions. Pb atoms in adjacent TCTPs in the plane of the projections are either at the same height along the short-cell dimension, in which case their TCTPs share faces, or shifted by ½ along this direction, in which case their TCTPs share edges. The two structures can be described with respect to the face-sharing linkages of their TCTPs. The structure of α-PbF_2 consists of corrugated sheets of face-sharing TCTPs, which interlock perpendicular to the c axis. In laurelite, the Pb2 TCTPs form three-membered clusters about the threefold axis that are propagated into trigonal cylinders by sharing faces in the direction of the c axis. The Pb1 and Pb3 TCTPs are linked into a three-dimensional framework with corresponding cylindrical voids.

Notwithstanding α-PbF_2, the tricapped trigonal prism is not a common coordination polyhedron among natu-

[1] A copy of Tables 2 and 3 may be ordered as Document AM-96-621 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

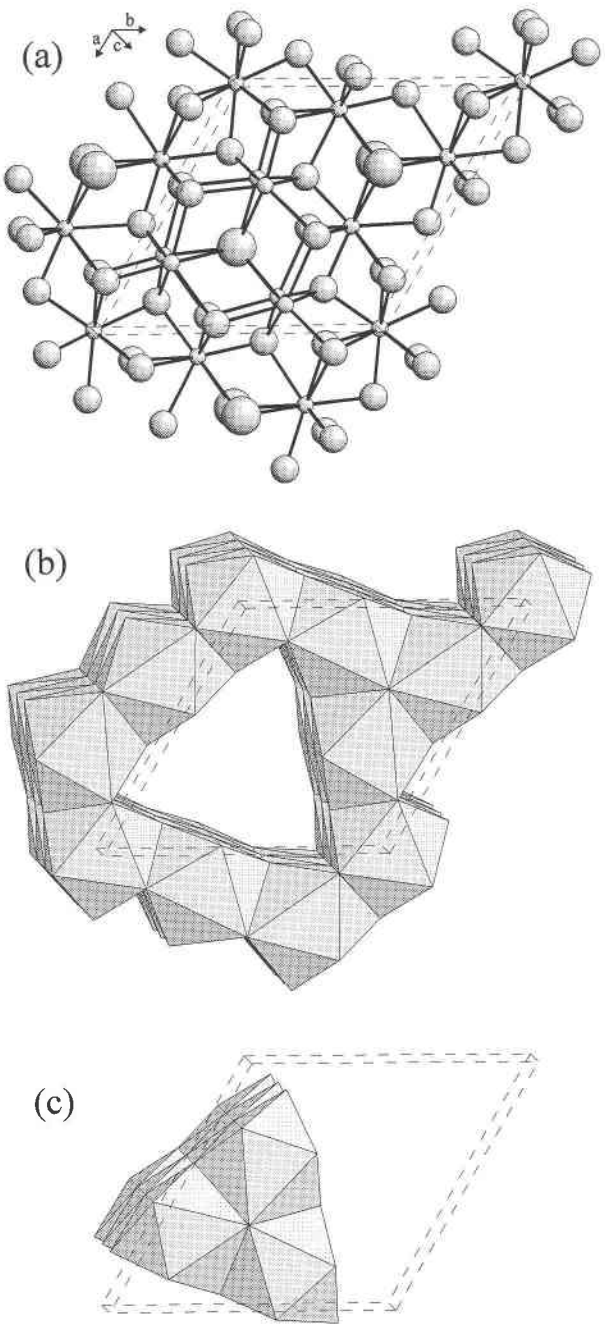

FIGURE 1. Crystal structure of laurelite viewed slightly off the *c* axis. The unit cell is outlined by the dashed lines. (a) Ball-and-stick diagram; small balls are Pb atoms, medium balls are F atoms, and large balls are Cl atoms. (b) Framework of face-sharing Pb1 and Pb3 TCTPs; three unit cells along *c* are shown. (c) Trigonal cylinder of face-sharing Pb2 TCTPs that fits in cylindrical void in framework.

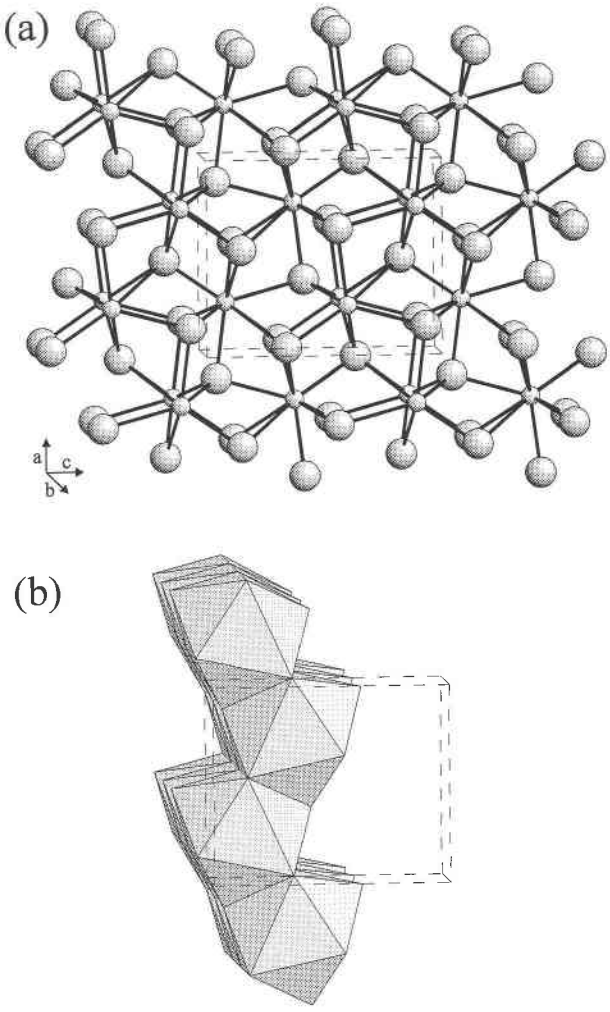

FIGURE 2. Crystal structure of α-PbF_2 (Boldrini and Loopstra 1967) viewed slightly off the *b* axis. The unit cell is outlined by the dashed lines. (a) Ball-and-stick diagram; small balls are Pb atoms and large balls are F atoms. (b) Corrugated sheet of face-sharing Pb TCTPs; three unit cells along *b* are shown.

rally occurring lead halides, being reported only for a phase, $Pb_2Fe^{3+}Cl_3(OH)_4 \cdot H_2O$, recently found as an alteration product of Etruscan metallurgical slags (Pasero et al. 1994). In most lead halides [e.g., laurionite (Cannillo et al. 1969), cotunnite (Nozik et al. 1976), paralaurionite (Merlino et. al 1993), fiedlerite-1*A* and fiedlerite-2*M* (Merlino et al. 1994), and penfieldite (Merlino et al. 1995)], Pb displays eightfold coordination in bicapped trigonal prisms. In matlockite, PbFCl (Pasero and Perchiazzi 1996), Pb is ninefold coordinated in monocapped square antiprisms.

Pb coordinations and the lone-pair effect

Pb1 and Pb2 in laurelite are each linked to seven F and two Cl atoms (Fig. 3). Pb1 and Pb2 are decidedly off-center within their coordination polyhedra, with the longer than normal Pb-(F,Cl) bonds on the same side of the polyhedra. This is attributed to the lone-pair effect in which the Pb lone-pair electron is localized on one side of the Pb atom (Moore et al. 1993). The Pb coordination in α-PbF_2 exhibits the lone-pair effect in a similar man-

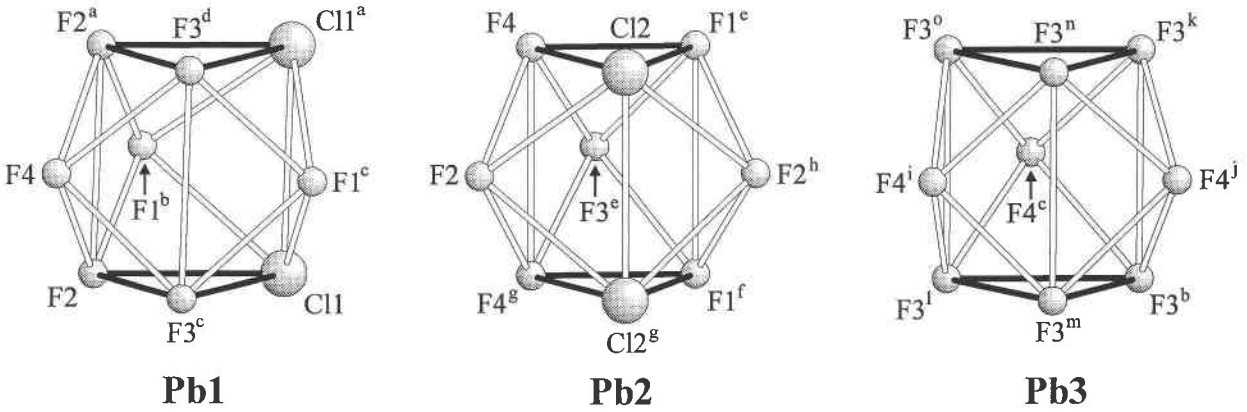

Figure 3. Coordination in the form of tricapped trigonal prisms (TCTP) around Pb1, Pb2, and Pb3 in laurelite. The edges corresponding to the trigonal prisms are shown in black. The lettered superscripts correspond to the symmetry codes given in Table 4.

ner. In laurelite, Pb3, which lies on a $\bar{6}$ axis, is linked to nine F atoms (Fig. 3) and does not exhibit the lone-pair effect.

Anion coordinations and the presence of OH

Cl1 and Cl2, lying on the threefold axes, are coordinated by six Pb atoms in a trigonal prismatic configuration. Three of the four independent F atoms (F1, F2, and F4) are tetrahedrally coordinated by four Pb atoms, with all Pb-F-Pb angles in the range 102–114°, whereas F3 is coordinated by five Pb atoms in a square pyramidal configuration. It is useful to compare the structural arrangement of anions in fiedlerite, another secondary lead halide that contains both F and OH (Merlino et al. 1994). In fiedlerite, the F atoms and the OH groups occur at distinct sites, the former surrounded by four Pb atoms, the latter linked on one side to three Pb atoms, with its H atom pointing in the other direction. The coordination of F atoms by four or five Pb atoms in laurelite, therefore, does not appear to allow substitution of OH for F and suggests the structural formula $Pb_7F_{12}Cl_2$.

Stacking defects

The residual peaks in the difference-Fourier synthesis are consistent with stacking defects involving successive domain slices perpendicular to the c axis in which the Pb atoms are shifted by $c/2$ with respect to corresponding Pb atoms in adjacent domains. At the boundaries between domains, the distance between neighboring Pb atoms within the TCTP tubes is $\frac{1}{2}c$. The effective result is $c/2$ vacancies in the stacking of the Pb atoms. In the small domains so created minor horizontal adjustments in the atomic positions of F and Cl would allow the anions that formerly made up the trigonal bases of the TCTPs to become the capping anions (at the same z level as the Pb) and the former capping anions to become the bases. Substitution of OH or H_2O would be possible at the F sites surrounding the Pb vacancies, with the H atoms accommodated in the vacancies. In this case, H_2O might be favored so as to compensate for local charge imbalance created by the local Pb^{2+} deficiency.

The stacking defects could help to explain both the H_2O content and the deficiency in Pb reported by Kampf et al. (1989). They reported the analysis Pb 82.0, F 13.0, Cl 3.6, OH 0.9 (H_2O 0.5), from which they derived the empirical formula $Pb_{0.94}[F_{1.63}Cl_{0.24}(OH)_{0.13}]$ on the basis of F + Cl + OH = 2. Considering that H_2O might be accommodated in the structure, we offer a new charge-balanced empirical formula, $Pb_{0.97}[F_{1.68}Cl_{0.25}(H_2O)_{0.07}]$.

Density-data revision

Kampf et al. (1989) determined a density of 6.2(1) g/cm³ for laurelite with the use of a pycnometer on a 9 mg sample. They compared this to the density of 6.52 g/cm³ calculated on the basis of their empirical formula and Z = 6. Kampf et al. (1989) attributed the discrepancy to the difficulty in handling the aggregates of needle-like crystals of laurelite and to small sample size. The ideal structural formula indicated in this study, $Pb_7F_{12}Cl_2$ (Z = 1), yields a calculated density of 8.03 g/cm³. The density calculated from the empirical formula of Kampf et al. (1989) and the new cell content (Z = 7) is 7.61 g/cm³. Our newly presented empirical formula containing H_2O, $Pb_{0.97}[F_{1.68}Cl_{0.25}(H_2O)_{0.07}]$, with Z = 7, yields a density of 7.77 g/cm³.

The availability of additional laurelite samples permitted a new density determination using a Berman balance. This yielded a measured density of 7.65(5) g/cm³ for a 13 mg sample consisting of very compact masses of parallel fibers.

Acknowledgments

The manuscript benefited from reviews by Frank C. Hawthorne of the University of Manitoba and John M. Hughes of Miami University (Ohio). Financial support by MURST (60% grant to S.M.) is acknowledged.

References cited

Boldrini, P., and Loopstra, B.O. (1967) Neutron diffraction investigation of orthorhombic lead(II) fluoride. Acta Crystallographica, 22, 744–745.

Brese, N.E., and O'Keeffe, M. (1991) Bond-valence parameters for solids. Acta Crystallographica, B47, 192–197.

Cannillo, E., Giuseppetti, G., and Tadini, C. (1969) Riesame della struttura della laurionite PbOHCl. Periodico di Mineralogia, 38, 395–402.

Kampf, A.R., Dunn, P.J., and Foord, E.E. (1989) Grandreefite, pseudograndreefite, laurelite, and aravapaite: Four new minerals from the Grand Reef mine, Graham County, Arizona. American Mineralogist, 74, 927–933.

Merlino, S., Pasero, M., and Perchiazzi, N. (1993) Crystal structure of paralaurionite and its OD relationships with laurionite. Mineralogical Magazine, 57, 323–328.

——— (1994) Fiedlerite: Revised chemical formula $[Pb_3Cl_4F(OH)\cdot H_2O]$, OD description and crystal structure refinement of the two MDO polytypes. Mineralogical Magazine, 58, 69–78.

Merlino, S., Pasero, M., Perchiazzi, N., and Gianfagna, A. (1995) X-ray and electron diffraction study of penfieldite: Average structure and multiple cells. Mineralogical Magazine, 59, 341–347.

Moore, P.B., Davis, A.M., Van Derveer, D.G., and Sen Gupta, P.K. (1993) Joesmithite, a plumbous amphibole revisited and comments on bond valences. Mineralogy and Petrology, 48, 97–113.

Nozik, Yu.Z., Fykin, L.E., and Muradyan, L.A. (1976) Crystal structure of cotunnite $PbCl_2$ determined more precisely by application of the neutron diffraction method. Soviet Physics Crystallography, 21, 38–40.

Pasero, M., Perchiazzi, N., Bigi, S., Franzini, M., and Merlino, S. (1994) OD character in PbFeCl, a new lead and iron (III) hydroxychloride with a novel structure-type. 16th General Meeting of the International Mineralogical Association, September 4–9, Pisa, Italy. Abstracts of Papers, 318.

Pasero, M., and Perchiazzi, N. (1996) Crystal structure refinement of matlockite. Mineralogical Magazine, 60, 833–836.

Sheldrick, G.M. (1985) SHELXS86. Program for the solution of crystal structures. University of Göttigen, Germany.

——— (1993) SHELXL-93. Program for the refinement of crystal structures. University of Göttigen, Germany.

Walker, N., and Stuart, D. (1983) An empirical method for correcting diffractometer data for absorption effects. Acta Crystallographica, A39, 158–166.

Manuscript received April 20, 1995
Manuscript accepted May 14, 1996