The joesmithite enigma: Note on the $6s^2$ Pb^{2+} lone pair

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Abstract

Joesmithite, end-member composition $PbCa_2Mg_3Fe_2^{3+}(OH)_2[Si_6Be_2O_{22}]$, is unique among clinoamphiboles in possessing same-cell space group $P2/a$. Since $P2/a$ is a subgroup of $C2/m$ and can be generated by suppressing inversion centers at (0 0 0, etc.) in the larger group, it is believed the lone pair-bond pair interaction by $6s^2$ Pb^{2+} at the "A" site in clinoamphibole conserves only the inversion centers at (¼ ¼ 0, etc.) and subsequent cell translation to $P2/a$. The $\{Cn\}$ ($n = 2, 3, 4, 6$) rotations and $\{m\}$ reflections can accommodate the stereoactive lone pair but $\{\bar{1}\}$ inversion cannot.

The Pb-"A" displacement is 0.601 Å, a typical displacement for Pb^{2+}. The Pb atomic position is well-ordered and not split, suggesting that the lone pair was stereochemically active during growth of joesmithite crystals.

Introduction

For all practical purposes, joesmithite is a rare clinoamphibole culled from its only reported locality in Långban, Sweden. Its composition $(Pb_{0.4} Ca_{0.6})_{\Sigma=1}^{2+}Ca_2$-$(Mg_{2.4}Fe_{0.6})_{\Sigma=3}^{2+}(Fe_{1.8}Al_{0.2})_{\Sigma=2}^{3+}(OH)_2[Si_6Be_2O_{22}]$, $Z = 2$, is highly peculiar, it being a beryllosilicate with (Pb,Ca) in the large "A" site that is vacant in most clinoamphiboles. The "A" site is centered at (0 ½ 0) for $C2/m$ clinoamphiboles. The species was first reported in detail by Moore (1968) and after assembling 1604 independent F_o, the full structure was reported by Moore (1969). The $R = 0.128$ was an acceptable discrepancy factor for the state of the art at that time and bond distances, site populations, and isotropic thermal parameters suggested the end-member composition $PbCa_2Mg_3Fe_2^{3+}(OH)_2[Si_6Be_2O_{22}]$. But neither this composition nor any additional site occupancy would degrade the symmetry group from $C2/m \rightarrow P2/a$, a simple "same cell" relationship decomposed by suppressing the inversion center at (0 0 0). In other words $P2/a \subset C2/m$.

The space group $P2/a$ is peculiar among the reported clinoamphibole structures, and Hawthorne (1983) in a review on the subject made a point of declaring its uniqueness. Yet the structure was topochemically that of a classic clinoamphibole with the exception of the "A" site at the origin. Moderate to strong intensity distributions and centric morphology required $P2/a$. What happened?

Discussion

Actually, joesmithite is no enigma. The lone pair associated with $6s^2$ Pb^{2+} at purported (0 ½ 0) forces a break in symmetry. Many tested examples in my laboratory show that the stereoactive lone pair at a special site need not break the symmetry of any point, allowing at least one degree of freedom such as $\{Cn\}$ ($n = 2, 3, 4, 6$) rotation or $\{m\}$ reflection. But residence on $\{\bar{1}\}$ inversion automatically either destroys the symmetry or splits Pb^{2+} into

two symmetrically disposed halves. Since all other sites in the joesmithite structure involve ions that are not stereoactive, Pb^{2+} is the most likely culprit for symmetry breaking. This remarkable group-subgroup relation was not earlier recognized because in Henry and Lonsdale (1969), the origin shift for $C2/m$ requires a translation of (¾ ¼ 0) to the second kind of inversion centers. The entire relation is summarized in Figure 1, which outlines the desired translations. Figure 2 portrays the displacements in the anion envelope of Pb^{2+} for joesmithite. All structural evidence indicates that the Pb atomic position is well-ordered and not split into two halves. This immediately suggests that the lone pair was stereochemically active at the onset of joesmithite's creation. Indeed, Moore (1969) stated "The 'A'-Be pair was coupled during incipient crystal growth, acting as a template and dictating the other cation distributions in the crystal." One may inquire about the displacement of the Pb^{2+} centroid from the purported inversion center of the first kind. This is $|(¼ ¼ 0)-(¼ 0.2836 0)|(b = 17.875$ Å$) = 0.601$ Å, a typical lone pair displacement for $6s^2$ Pb^{2+} due to interaction with the neighboring bond pairs. Such a displacement along with atomic number 82 for Pb leads to a pronounced appearance of $P2/a$ in lieu of $C2/m$.

An interesting feature concerns the "A" site itself. Chemical crystallographic evidence suggests mixing of (Pb,Ca) at this site, that is, a lone-pair cation (Pb^{2+}) in solution with a cation stripped of all its valence electrons (Ca^{2+}). This is analogous to the Pb-K segregation in synthetic KPS, $Pb_2O(Pb_2K_2)[Si_8O_{20}]$ ($R = 0.034$), where half-occupied Pb(2) and K have Pb(2)-K 0.59-Å separation (Moore et al., 1985). The driving mechanism for this separation can be attributed to lone pair–bond pair interactions for Pb^{2+} but no such interactions for K^+. In joesmithite, a similar splitting may exist, but such proof will not be easy since $82 \times 0.40 = 32.8$ electrons for Pb and
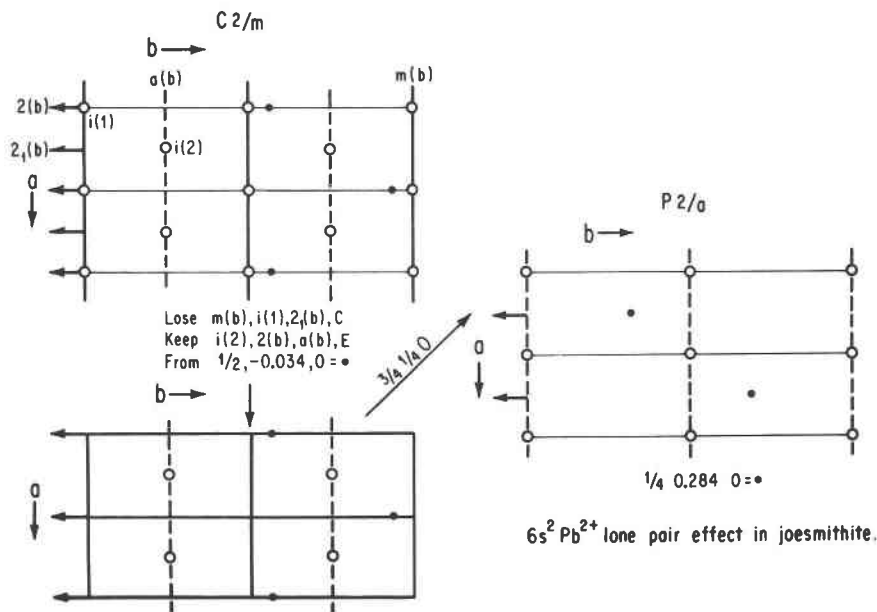
Fig. 1. Symmetry breaking in joesmithite. Top left, the space group elements and symbols of equivalences in $C2/m$ with dot denoting Pb^{2+} displaced off "A" (0 ½ 0) leading to equivalences compatible with displacement (lower left). Translation of cell by (¾ ¼ 0) gives the desired $P2/a$ on right.

$20 \times 0.60 = 12$ electrons for Ca. This would require careful re-examination of the entire chemical crystallography of joesmithite, which is already chemically very complex. It is predicted that a Pb-Ca separation would occur in a manner similar to Pb-K in KPS. This lone-pair cation–inert-core cation splitting could have some remarkable consequences, e.g., in disruption of K^+, Na^+, and Ca^{2+} pathways in living organisms that may explain in part Tl^+, Pb^{2+}, Bi^{3+}, Sb^{3+}, As^{3+}, etc., "heavy metal" toxicities and ensuing neuropathies. This, of course, is highly speculative but may lead to potentially fruitful further investigation.

I suggest that this phenomenon will be found to be generally operative in crystals where Pb^{2+} occurs at purported $\{\bar{1}\}$ point symmetry. Examination of sulfosalt structure types with lone-pair cations should also reveal pleasant surprises and may explain some of their complex crystal structures, which also possess symmetry groups of low order.

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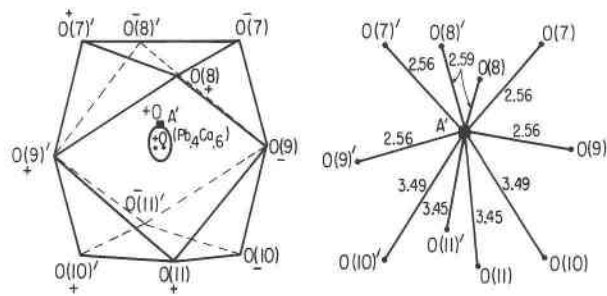
Fig. 2. Anion coordination polyhedron about (Pb,Ca) in joesmithite. Distances are in Å. The distorted "A" site leads to six "short" distances and four "long" distances, suggesting the approximate location of the lone pair in the polyhedron. This is an axonometric projection, a is W to E, b is S to N, c toward reader. Coordinates are from Moore (1969) and + and − are above and below A' centroid. The equivalence for anions: $' = \frac{1}{2} - x, y, \bar{z}$.