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The role of rigid unit modes in negative thermal expansion

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Abstract

The rigid unit mode (RUM) model provides a valuable computational method to investigate correlations of transverse thermal motions of atoms important in negative thermal expansion (NTE) materials. We report here detailed RUM calculations of ten framework oxide structures that have been studied for their negative (or ultra low) thermal expansion properties. The results negate any simple and direct correlation between presence or absence of RUMs in a structure and its NTE property. All the structures considered can be viewed as networks of polyhedral connected by corners only. All evidence supports the importance the transverse motion of the atoms at the corners, but NTE does not correlate well with the presence RUMs for the polyhedra.

Keywords: Negative thermal expansion; Rigid unit modes; Vibrational modes; Oxides

1. Introduction

The RUM model is closely associated with a long history of studies on crystallographic structures, phase transitions and physical properties of framework silicates [1]. It has been recognized that existence of $SiO_{4/2}$ tetrahedra is a conspicuous structural feature in this type of solid. These tetrahedra are adequately ideal and rigid to be considered the common building block in many 3-D networks of different topologies, and they exhibit little change in shape or size through phase transitions. Lattice dynamic studies of quartz [2] had also drawn attention to the fact that soft modes of displacive phase transitions in these structures should involve the tetrahedra tilting as rigid units because dynamic atomic motions associated with the soft mode correspond to static displacements associated with this kind of phase transition. It was realized that the idea of lattice vibrations in which $SiO_{4/2}$ tetrahedra tilt as basic units has important quantitative implications, and a modeling method to generalize the approach was developed [3] and implemented through the computer program CRUSH [4].

In this RUM model a framework structure is viewed as a 3-D periodic network of interconnecting corner-sharing polyhedra, which are treated as *rigid units*, a classic mechanical structure with a mass, a moment of inertia, three translational degrees of freedom, and three vibrational degrees of freedom. No other forces or interactions exist between these rigid units except the rigid connectivity between neighboring connected units. Lattice vibration waves supported by this kind of idealized network structures (RUMs) are illustrated in Fig. 1.

After publication on the NTE property of ZrW_2O_8 [5] through a large temperature range, Pryde et al. [6] applied the RUM method to ZrW_2O_8 and found a surprisingly large number of RUMs. It was proposed that these RUMs were responsible for NTE in ZrW_2O_8. In this model NTE is caused by the transverse thermal motion of oxygen in the Zr–O–W linkages as originally proposed [5,7]. However, the RUM model further assumes that the $ZrO_{6/2}$ octahedra and $WO_{4/2}$ tetrahedra are rigid, and rocking motions of these polyhedra describe the correlations between the thermal motions of the oxygen atoms. These vibration modes are expected to be of low frequency/energy; with increasing temperature they are excited to shrink the lattice.

More recently, many more oxides have been found to show NTE [8]. Thus, we now have the opportunity to survey many oxides with different stoichiometries and structures to investigate the importance of RUMs for

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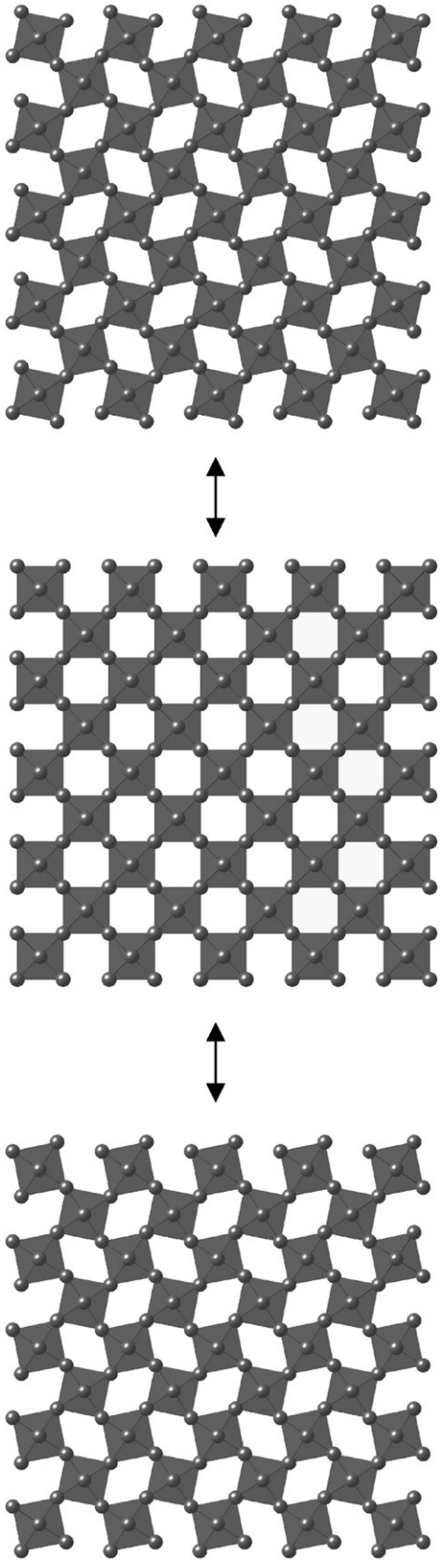

Fig. 1. Rocking motion of octahedra for a rigid unit mode (RUM) in a ReO_3 type structure.

NTE. CRUSH calculations have been used to determine which of the structures have RUMs.

2. Results

The two most common polyhedra building blocks in framework oxide structures are tetrahedra and octahedra. If all polyhedra are corner sharing with all oxygen in two-fold coordination, the generic composition of a framework structure is $A_xM_yO_{3x+2y}$, where A and M are the octahedral and tetrahedral cations, respectively. Five simple examples are known to exist: AO_3, AM_2O_7, $A_2M_3O_{12}$, AMO_5, and MO_2. These five families have been systematically investigated for NTE [7,8,10–20].

2.1. MO_2 family

The large family of framework silicates and aluminophosphates are the well known and well studied $MO_{4/2}$ networks, which consist of almost rigid and ideal $SiO_{4/2}$ tetrahedra (or $AlO_{4/2}$ and $PO_{4/2}$ tetrahedra) interconnecting to each other by sharing corners. Most of these framework structures contain interstitial ions or molecules, which significantly impact thermal expansion properties. Those without interstitial ions or molecules frequently exhibit NTE [10–12].

The aluminophosphate, $AlPO_4$-17, is comprised of alternating, corner-sharing $AlO_{4/2}$ and $PO_{4/2}$ tetrahedra (Fig. 2). The negative thermal expansion property of this material has been predicted from the results of computer simulation [9], and then determined experimentally. It is shown to have an unusually large negative linear thermal expansion coefficient (-11.7×10^{-6}/K) over the temperature range 18–300 K [10]. The structure of $AlPO_4$-17 is hexagonal (space group $P6_3/m$) with strong NTE along both the a and c axes. We find that RUMs exist for all $\{\xi,\eta,0\}$ vectors in this structure.

CIT-5 (Fig. 3) is a siliceous zeolite with an orthorhombic structure in space group $Im2a$ with the point group being C_{2v} ($mm2$). The irreducible part of the Brillouin zone is therefore only $\frac{1}{8}$ of the entire Brillouin Zone. A $50\times50\times50$ 3-D grid occupying the parallelepiped defined by wavevectors $(0.5,0,0)$, $(0,0.5,0)$ and $(0,0,0.5)$ was therefore used to generate a list of K points in search of possible RUMs, which we find in this structure for all wavevectors on the plane $(0,\xi,\eta)$. The thermal expansion coefficient for siliceous CIT-5, however, is relatively large and positive (1.49×10^{-5}/K) over temperature range 373–973 K [12].

RUMs are known to exist in the common crystalline forms of SiO_2: quartz, tridymite, and cristobalite. In fact, we know of no example of a tetrahedral MO_2 structure without RUMs.

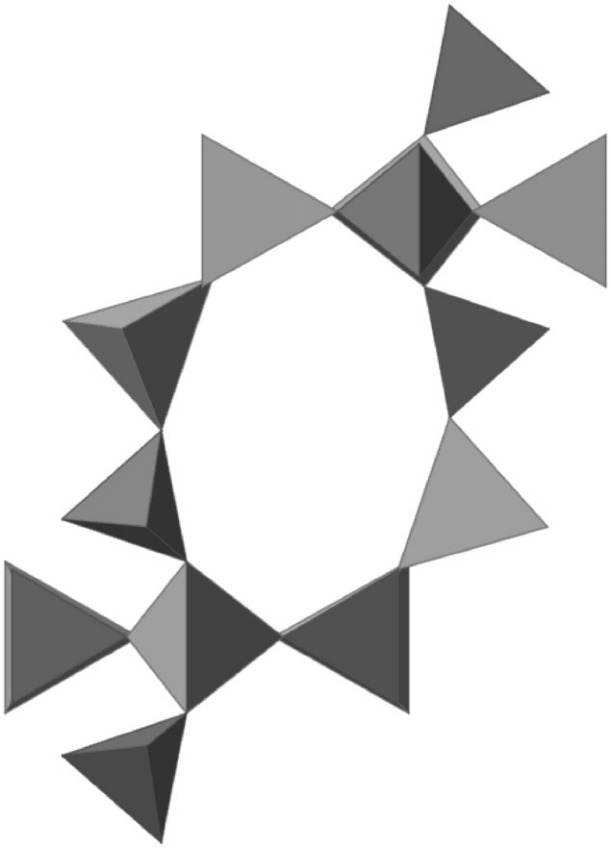

Fig. 2. The structure of $AlPO_4$-17 with corner sharing $AlO_{4/2}$ and $SiO_{4/2}$ tetrahedra.

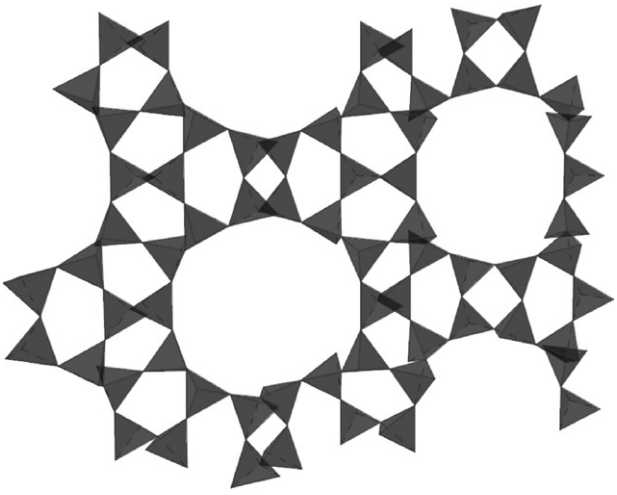

Fig. 3. The structure of CIT-5 as corner sharing $SiO_{4/2}$ tetrahedra.

2.2. $A_2M_3O_{12}$ family

Two distinctly different connectivities are known for this formula. One with rhombohedral symmetry is known for the compounds $ANbP_3O_{12}$ where A may be Ti, Zr, or Hf [13,14]. We find no RUMs for this structure, but NTE behavior is very much in evidence. The thermal expansion is, however, very anisotropic and very nonlinear.

The other $A_2M_3O_{12}$ framework structure (Fig. 4) is known for a large family of compounds, and it can exist in either orthorhombic or monoclinic symmetry. In this structure each $AO_{6/2}$ octahedron shares each of its corners with a $MO_{4/2}$ tetrahedron, and each $MO_{4/2}$ tetrahedron shares each of its corners with an $AO_{6/2}$ octahedron. The A cation can be either $+3$ (e.g., $Sc_2W_3O_{12}$) or $+4$ (e.g., $Zr_2WP_2O_{12}$). The fact that this structure cannot be constructed from ideal octahedra and tetrahedra suggests that RUMs cannot be present. The best studied compounds of this family are orthorhombic $Sc_2W_3O_{12}$ [15], $Y_2W_3O_{12}$ [16], $Lu_2W_3O_{12}$ [17], and $Zr_2WP_2O_{12}$ [18] with NTE covering a wide temperature range (-2.2×10^{-6}/K over 10–1073 K for $Sc_2W_3O_{12}$, -3.0×10^{-6}/K over 50–450 K for $Zr_2WP_2O_{12}$, -6.8×10^{-6}/K over 127–627 K for $Lu_2W_3O_{12}$, and -7.0×10^{-6}/K over 15–1373 K for $Y_2W_3O_{12}$). Isostructural $Sc_2Mo_3O_{12}$ shows NTE above a phase transition where it possesses orthorhombic symmetry. Below this phase transition (Fig. 5) where $Sc_2Mo_3O_{12}$ possesses monoclinic symmetry, positive thermal expansion is observed [18,19].

The point group for this orthorhombic structure of space group *Pnca* is $D_{2h}(mmm)$; therefore, a $50\times50\times50$ 3-D grid of K points ($0\sim0.5$, $0\sim0.5$, $0\sim0.5$) was used for CRUSH calculations to search for RUMs. None of the vibrational modes of this list of wavevectors has zero frequency. Therefore, we conclude no RUMs exist in this network structure type regardless of whether the symmetry is orthorhombic or monoclinic.

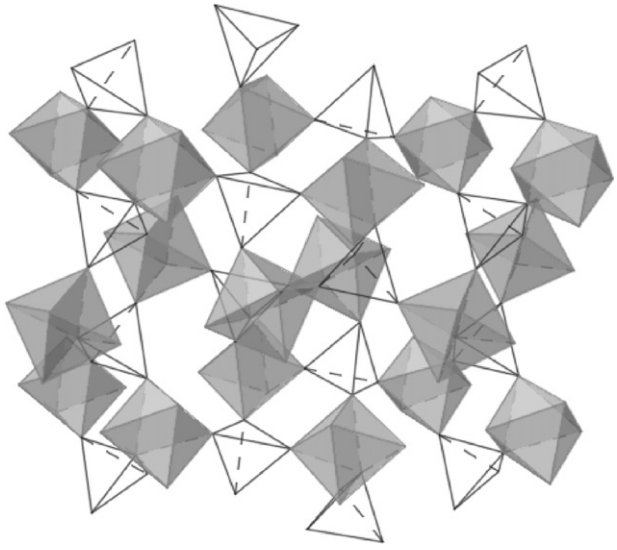

Fig. 4. The $Sc_2W_3O_{12}$ network as corner-sharing $ScO_{6/2}$ octahedra and $WO_{4/2}$ tetrahedra.

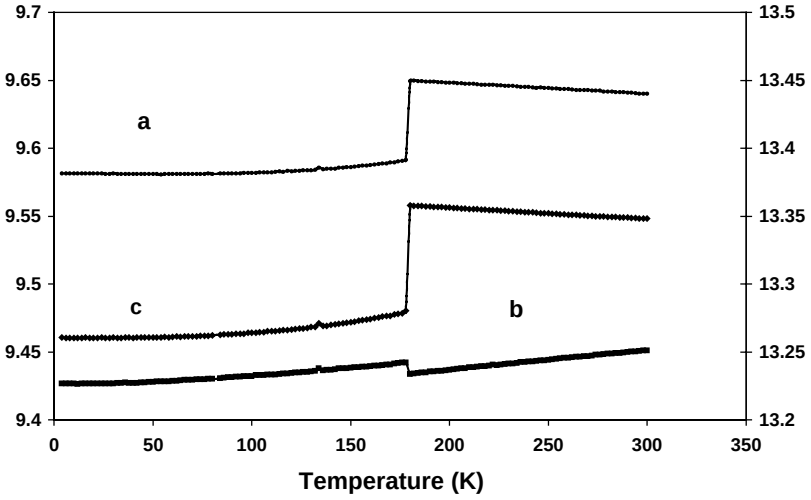

Fig. 5. The cell dimensions of $Sc_2Mo_3O_{12}$ vs. temperature, orthorhombic at high temperature and monoclinic at low temperature with β angle very close to 90°. The left scale is for a and c, and the right scale is for b.

2.3. AMO_5 family

From the overall stoichiometry two possible combinations are possible: two +5 cations or one +4 cation plus one +6 cation. So far only $A^{5+}M^{5+}O_5$ compounds have been studied for thermal expansion. The A cations can be Nb, Ta, Mo, or V; the M cations can be P, V, As, P, S, Mo. They form a large family of compounds with corner-sharing interconnecting $AO_{6/2}$ octahedra and $MO_{4/2}$ tetrahedra. Several different networks are known in this family. Thermal expansion has been studied for two networks of this family, and NTE behavior was found in all cases studied [20–22]. In these network structures each $AO_{6/2}$ octahedron share corners with four $MO_{4/2}$ tetrahedra and 2 other octahedra, and each $MO_{4/2}$ tetrahedron shares corners with four $AO_{6/2}$ octahedra. Both of these network structures have displacive transitions as a function of temperature. For one structure (Fig. 6), the symmetry is tetragonal above (space group $P4/nmm$ and point group D_{4h}, $4/mmm$) and below (space group $P4/n$ and point group C_{4h}, $4/m$) this transition. The high-temperature tetragonal phases of $NbOPO_4$ and $TaOPO_4$ show NTE [18,20]. Our RUM modeling indicates that no RUMs exist in lower temperature tetragonal phase, but all $\{0, 0, \xi\}$ wavevectors possess RUMs in the higher-temperature, higher-symmetry phase. The a and b axes only show NTE behavior in the high temperature phase, whereas there is no NTE behavior below the transition. The transition itself can be described as a freezing out of RUMs as the temperature is decreased. There is apparent confirmation of the importance of the RUMs in this case, but the volume thermal expansion remains positive even when the RUMs are present.

The other AMO_5 structure that has been studied is orthorhombic (space group $Pnma$ and point group D_{2h}, mmm) above the transition and monoclinic (space group $P2_1/c$ and point group C_{2h}, $2/m$) below the transition [21,22]. Our RUM modeling here indicates that no RUMs exist in lower temperature monoclinic phase, but there is one RUM at $(\frac{1}{2}, 0, \frac{1}{2})$ in the higher temperature orthorhombic phase. However in this case, one axis shows NTE behavior unchanged through the transition. Above the transition all three axes show NTE behavior. Thus in this case, there is some correlation between the presence of RUMs and NTE behavior, especially considering that the volume thermal expansion is positive without a RUM and negative with a RUM.

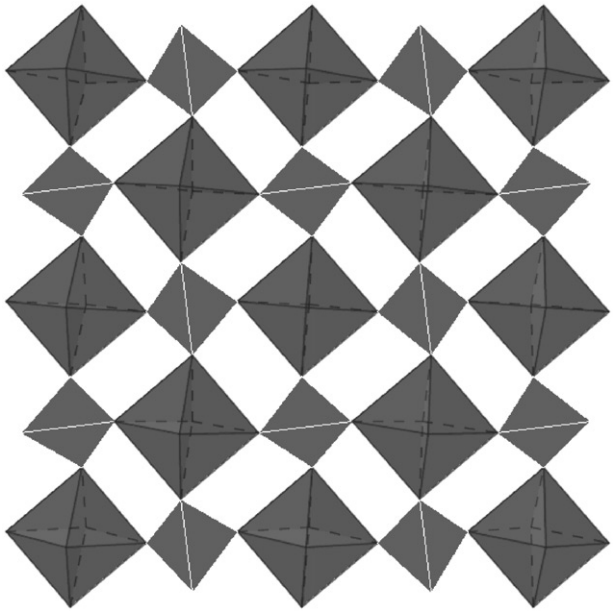

Fig. 6. The $NbOPO_4$ structure viewed down the tetragonal c-axis.

These results are consistent with the fact that RUMs only appear when a structure is underconstrained, most often as the symmetry of a structure is high enough to reduce the independent number of constraints (or polyhedra linkages). More interestingly there is a similarity between this system and that of α–β quartz, in terms of existence of RUMs. In both cases there are displacive phase transitions and appearance of negative thermal expansion in higher temperature phases. It is likely that just as for SiO_2 one of the RUMs in the AMO_5 phases is the soft mode driving displacive phase transitions in this system.

2.4. AO_3 network

Several different network structures are known in this family, but apparently thermal expansion has only been studied in one of these. This cubic network consists of purely corner-sharing $MO_{6/2}$ octahedra (Fig. 1). Our CRUSH calculations show RUMs exist for all wave-vectors $\{\frac{1}{2}, \frac{1}{2}, \zeta\}$, corresponding to "rocking motions" of octahedra along each of three axes. This ideal structure exists for ReO_3, which has low but positive thermal expansion [23], and for TaO_2F, which we find to have a very low thermal expansion [24].

2.5. AM_2O_7 and AM_2O_8 families

The AM_2O_7 family is known to exhibit NTE for several compositions, but CRUSH calculations have shown that no RUMs are present [6]. There is, however, experimental evidence for quasi-RUMs in this structure in the ideal form [25]. In this structure each $AO_{6/2}$ octahedron shares corners with six $MO_{4/2}$ tetrahedra, and each $MO_{4/2}$ tetrahedron shares corners with three $AO_{6/2}$ octahedra and one other $MO_{4/2}$ tetrahedron. These materials, such as ZrV_2O_7, typically undergo phase transitions as a function of temperature. NTE behavior may be present in the higher-temperature, higher-symmetry cubic phases [7], but it disappears below the phase transition.

If the $MO_{4/2}$ tetrahedra in this network only share corners with three $AO_{6/2}$ octahedra and leave one corner linkage free, the resulting structure is that of cubic α-ZrW_2O_8, which is shown to experience large isotropic thermal expansion over a wide temperature range from close to 0 K up to about 1500 K [5,26]. Isostructural $Zr(W,Mo)_2O_8$ phases and HfW_2O_8 have similar NTE properties [27,28] (Fig. 7).

RUM modeling showed that many RUMs are present in ZrW_2O_8 structure, which however do not contain any special symmetry K points [6]. For all other framework oxide structures except the ideal tridymite structure, RUMs appear as planes of special symmetry points [1]. This unique feature of ZrW_2O_8 appears to be a consequence of its unique structure among all the framework oxides considered. The fact that some polyhedra corners are linkage free makes this structure the most underconstrained.

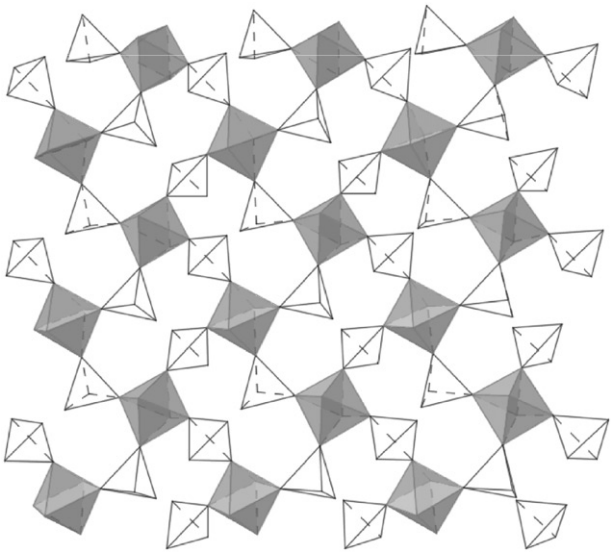

Fig. 7. Structure of ZrW_2O_8 as a network of corner-sharing $ZrO_{6/2}$ octahedra and $WO_{4/2}$ tetrahedra.

3. Discussion and conclusions

RUM modeling results are summarized in Table 1. Obviously, the presence of RUMs is not a reliable indicator for NTE. Some correlation between RUMs and NTE apparently exists. For example, there are several examples of compounds with NTE behavior above a phase transition where RUMs exist, with this NTE behavior disappearing below the phase transition where RUMs have also disappeared. However, the AM_2O_7 and $A_2Mo_3O_{12}$ families have phase transitions with NTE behavior only above the transition, but here there are no RUMs below or above the transitions.

The $A_2W_3O_{12}$ family well illustrates that strong NTE behavior can exist without RUMs. Strong NTE behavior has been observed over very large temperature ranges for $Sc_2W_3O_{12}$, $Lu_2W_3O_{12}$ and $Y_2W_3O_{12}$ [15–18]. However, NTE behavior is not observed in the $A_2W_3O_{12}$ family if A is smaller than Sc. One can thus argue that NTE behavior can only exist in this family with the greater flexibility of the larger polyhedra. For the isostructural $A_2Mo_3O_{12}$ family, NTE behavior only exists in the orthorhombic form found above a phase transition. Below this transition (Fig. 5), the monoclinic phase shows positive thermal expansion. Presumably, vibrational modes in the orthorhombic phase that cause NTE are frozen out in this monoclinic phase, but these are not RUMs.

Table 1
Summary of RUM analysis for framework oxides

Structure families	Framework connectivity	Crystal symmetry	RUM	NTE
ReO_3 type	Pure octahedra corner-sharing network	C	Yes	No
AMO_5 types	Octahedra:tetrahedra = 1:1	T, O, M	Yes and no	Yes
$A_2M_3O_{12}$ types	Octahedra:tetrahedra = 2:3	R, O, M	No	Yes
ZrW_2O_8	Octahedra:tetrahedra = 1:2	C	Yes	Yes
ZrV_2O_7			No	
MO_2 types	Pure tetrahedra corner-sharing network	C, H, T, O	Yes	Yes

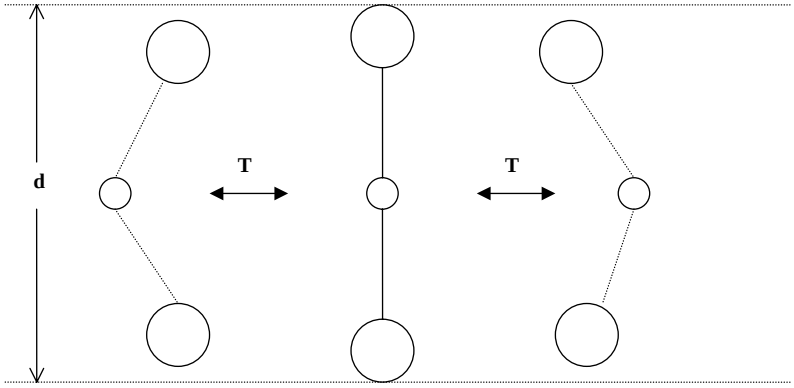

Fig. 8. Apparent decrease of interatomic distances due to thermal vibration of 2-coordinated oxygen atoms.

All of the oxides so far discussed are based on cation polyhedra sharing corners only. However, we also have a few cases where it is the cation, instead of the anion, that is in two-fold coordination. In the structure found for Cu_2O and Ag_2O, the cation is in two-fold coordination to oxygen. Both compounds show NTE behavior [23,29,30]. RUMs obviously exist in this structure because we have the same connectivity and symmetry as in cristobalite SiO_2 for which RUMs have been established [1]. However, the NTE behavior of the O–Cu–O linkage in $CuScO_2$ has recently been found to be much stronger than in Cu_2O [31]. The $CuScO_2$ structure is rigid without RUMs. Thus, we have another example where NTE behavior does not correlate with RUMs. Furthermore, a very recent EXAFS study of Ag_2O indicates that RUMs are not the cause of NTE behavior in this compound [30].

Decades ago crystallographers began correcting bond distances for the thermal motion (Fig. 8) of atoms [32]. On so doing they found that the apparent NTE behavior of some bond distances disappeared, especially for Si–O bond distances. This correction is especially significant for transverse thermal motion of an atom in two-fold coordination. There must be correlation of this motion among different atoms, but the RUM model is not completely adequate to describe this correlation, except possibly in the case of very rigid polyhedra, such as $SiO_{4/2}$. A RUM-like model can still be employed if the only small polyhedra distortions are required for the rocking motions of the polyhedera [33]. More investigation is required to determine if NTE behavior in structures without RUMs can be attributed to such quasi-RUMs.

Examples of NTE behavior without two-fold coordination do exist. Strongly anisotropic structures can have positive thermal expansion in some directions and NTE behavior in other directions [34]. This can give low volume thermal expansion, which can be negative as in the case of β-eucryptite. Such a mechanism has never been known to give a strong negative volume expansion in an intrinsic way. However, microcracking effects in strongly anisotropic materials can give strong volume NTE, which is extrinsic in nature.

There are other mechanisms for strong NTE. Strong NTE behavior is found for tetragonal $PbTiO_3$ [35]. The $TiO_{6/2}$ network here is that shown in Fig. 1. Thus, one might expect that the NTE behavior is related to the RUM depicted in Fig. 1. However, that is not the case. There is no atom in two-fold coordination in the $PbTiO_3$ structure. The cubic-to-tetragonal transition in $PbTiO_3$ is not based on the rocking motion shown in Fig. 1. The tetragonal distortion of $PbTiO_3$ is instead based on distortions of both the $TiO_{6/2}$ and $PbO_{12/4}$ polyhedra. The NTE behavior in $PbTiO_3$ results from these polyhedra becoming more regular with increasing temperature. This is an interesting example where the longer Ti–O and Pb–O bond distances show genuine NTE behavior. The shorter Ti–O and Pb–O distances are at the same time showing a weaker positive thermal expansion. Thus, the average Ti–O and Pb–O distances

decrease until the polyhedra become regular in the cubic structure. This mechanism gives NTE behavior below a phase transition whereas the NTE behavior based on transverse thermal motion is above a phase transition in those cases where there is a phase transition.

Acknowledgments

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