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Origin of the negative thermal expansion in ZrW_2O_8 and ZrV_2O_7

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Abstract. The negative thermal expansion recently observed over a wide range of temperatures in ZrW_2O_8 may be attributed to the existence of low-frequency phonon modes which can propagate with no distortions of the WO_4 tetrahedra and ZrO_6 octahedra, the so-called ‘rigid unit modes’. Using methods developed for the study of similar modes in silicates we have located the surfaces of these modes in wave-vector space. The rigid-unit mode interpretation accounts for the weak effect of the 430 K structural phase transition on the negative thermal expansion, provided that the disordered phase does not involve formation of W_2O_7 and W_2O_9 complexes. On the other hand, the crystal structure of the related material ZrV_2O_7 is cross braced by pairs of linked tetrahedra and is therefore significantly less flexible. In this case a qualitatively different mechanism may be responsible for the negative thermal expansion observed in ZrV_2O_7 .

1. Introduction

Recently the existence of negative thermal expansion in ZrW_2O_8 has been reported to exist over the complete range of stability of this material, even though there is a structural phase transition in the middle of this range [1]. Although there are a number of other materials that have negative thermal expansion along one axis, including the silicates quartz [2] and cordierite [3], and some zeolites [4], the fact that the crystal structure of ZrW_2O_8 is cubic in both phases [1] means that the negative thermal expansion is isotropic. A similar negative thermal expansion has also been found to exist at high temperatures in the related material ZrV_2O_7 [5]. The ability to synthesize materials with isotropic negative thermal expansion at all temperatures will facilitate the development of new high-performance composite materials with tuneable thermal properties.

Mary *et al* [1] attributed the negative thermal expansion in ZrW_2O_8 to the existence of low-energy Zr–O–W transverse vibrations. The existence of fairly stiff WO_4 and ZrO_6 polyhedra linked at corners (figure 1) implies that the transverse motion of an oxygen along a Zr–O–W linkage will necessarily cause counter-rotations of the linked WO_4 and ZrO_6 polyhedra. This sort of cooperative motion, where the polyhedra can rotate without distortion, is called a ‘rigid unit mode’ (RUM) [6–9], and will clearly have a low energy or

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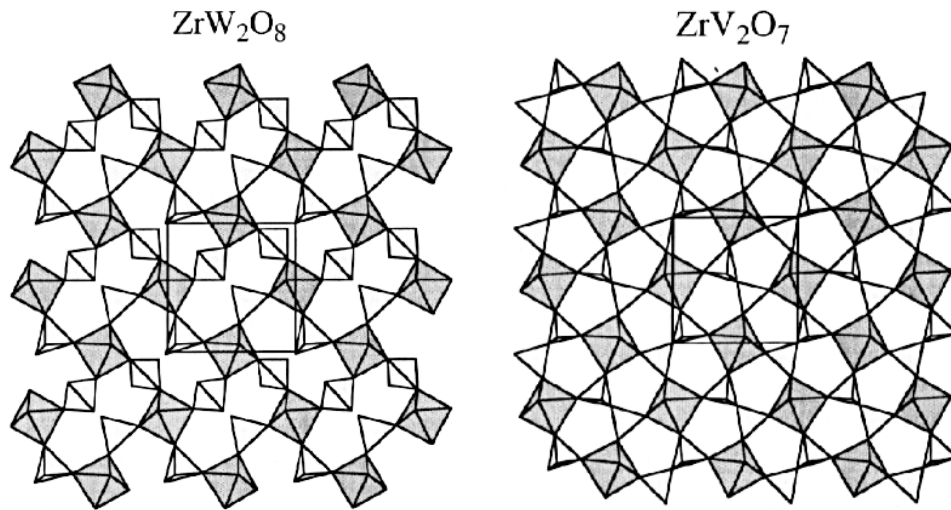


Figure 1. Crystal structures of ZrW_2O_8 and ZrV_2O_7 viewed down $[100]$, showing the ZrO_6 octahedra, and the WO_4 and VO_4 tetrahedra, as shaded polyhedra. Both are drawn to the same scale.

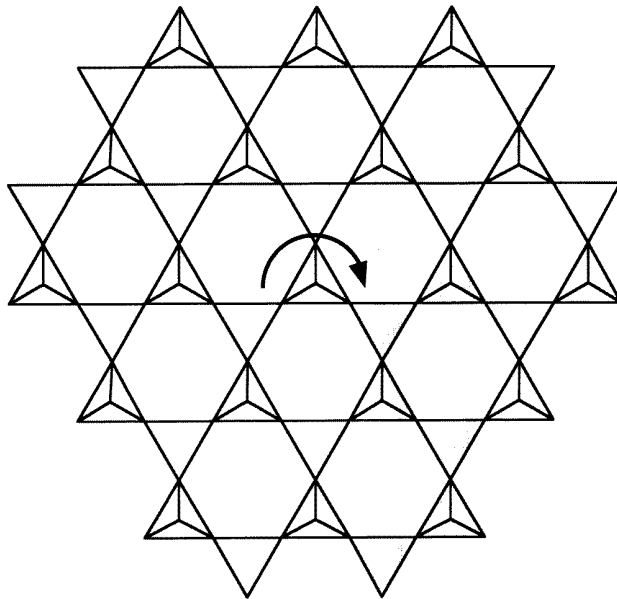


Figure 2. An array of linked triangles as found in tridymite. Rotation of one triangle causes the local environment to be pulled inwards.

frequency (these are called ‘floppy modes’ in the literature on the low-energy excitations in glasses). The RUM model for negative thermal expansion [8, 9] is illustrated in figure 2, which shows a two-dimensional network of linked triangles representing the arrangement of planes of linked tetrahedra in the tridymite and cristobalite phases of silica. It is easy

to see from this figure that the rotation of one of the triangles in the middle of this section will drag along with it, and inwards, its neighbouring triangles. The net effect will be a reduction in the total area (volume) that will be proportional to θ^2 . In a dynamic situation the triangles will be continuously rotating backwards and forwards due to the propagating RUM phonons, leading to an equilibrium value

$$\langle \theta^2 \rangle \propto k_B T / \omega^2$$

where ω is the frequency of the rotational phonon. This will be true for each triangle, not just one isolated triangle. Thus there will be a net volume change

$$\Delta V \propto -\langle \theta^2 \rangle \propto -k_B T \sum a_k \omega_k^{-2}$$

where we now sum over all rotational phonons with wave vector k and include a weighting factor a_k for each phonon that reflects the rotational component of each RUM. Thus the existence of the RUMs automatically provides a geometrical mechanism for a negative thermal expansion which is not restricted to any limited range of temperatures. Moreover, since the frequencies ω_k of the RUMs will be relatively low, the weighting of the RUM contributions to the overall thermal expansion will be relatively high. In certain cases this negative expansion may outweigh the positive thermal expansion of the chemical bonds (Si–O, W–O or Zr–O) in the rigid units.

Although the model described above is usually interpreted in relationship to the possible existence of zero-frequency RUMs, studies of complex silicates have highlighted the importance of vibrational modes where there is a minimal but finite distortion of the structural polyhedra. These are called quasi-RUMs (QRUMs), and there can be many more QRUMs than actual RUMs in a structure [8]. The energy associated with the distortions of the units may be substantially smaller than the energy associated with flexing of the bond angles at the linkages between polyhedra, so from an energetic perspective the QRUMs can play the same role as RUMs, which may be particularly important in the consideration of thermal expansion.

2. The existence of RUMs in ZrW_2O_8

Our first objective is to deduce whether any RUMs are allowed in the ZrW_2O_8 structure. The standard approach [6–9] is to count the number of degrees of freedom, F , and the number of constraints, C . With no other considerations the number of RUMs will be equal to $F - C$. In ZrW_2O_8 the two tetrahedra and one octahedron give $F = 18$ per formula unit. The constraints are counted by noting that there are three constraint equations per linkage. Each octahedron has six linkages and each tetrahedron three (one of the W–O bonds is non-bridging), so when we account for the sharing of the constraints associated with a single linkage by two rigid units, we have $C = 18$ per formula unit. Thus $F - C = 0$, so there may not actually be any low-frequency phonon modes allowed by the topology of the structure. However, a missing ingredient is the crystal symmetry, which generally decreases the actual number of *independent* constraints [6, 7, 9]. Indeed, any framework silicate will also have $F - C = 0$ by the standard counting scheme, but symmetry ensures that most framework silicates have RUMs with wave vectors on lines or planes in reciprocal space, and in some cases there can be one RUM or more for each wave vector [7, 8]. Other examples have RUMs on exotic curved surfaces in wave-vector space [10].

We have used a dynamical matrix method [6, 9, 11] to calculate the number of RUMs in the ordered $P2_13$ structure of ZrW_2O_8 [1]. In this approach the polyhedra are treated as rigid units, and the atoms that are shared between two polyhedra are split into two halves,

one associated with each of the two linked polyhedra. The split atoms are hindered from separating by a harmonic force that formally resembles the force required to distort the polyhedral units [7]. In this model the RUMs are calculated to have zero frequency. The calculations showed that, unlike many crystalline silicates [8], there are no RUMs for wave vectors at any special points in the Brillouin zone or along special symmetry directions. We therefore used a search method that can detect RUMs for any wave vectors in a two-dimensional section or three-dimensional volume of reciprocal space. The results of this search are shown in the [100] and [111] sections of reciprocal space in figure 3(a). The curves on these sections represent the loci of wave vectors with a RUM. The complete three-dimensional RUM surface we have calculated is shown in figure 3(b). It should be noted that this is the first example of such a complex surface of RUMs we have found, and it is the more striking for the fact that it does not contain any symmetry points. Analysis of the eigenvectors of the RUMs shows that they are equivalent to the acoustic modes in the limit of small wave vector. In the special case of ideal tetrahedra and octahedra all the elastic constants were calculated to be zero, which indicates some intrinsic flexibility in the crystal volume. The eigenvectors of the RUMs quickly change from the pure acoustic

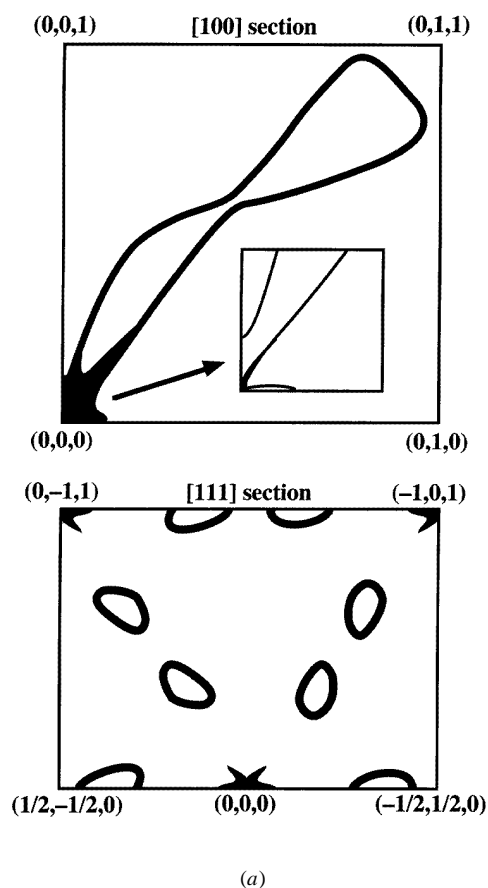
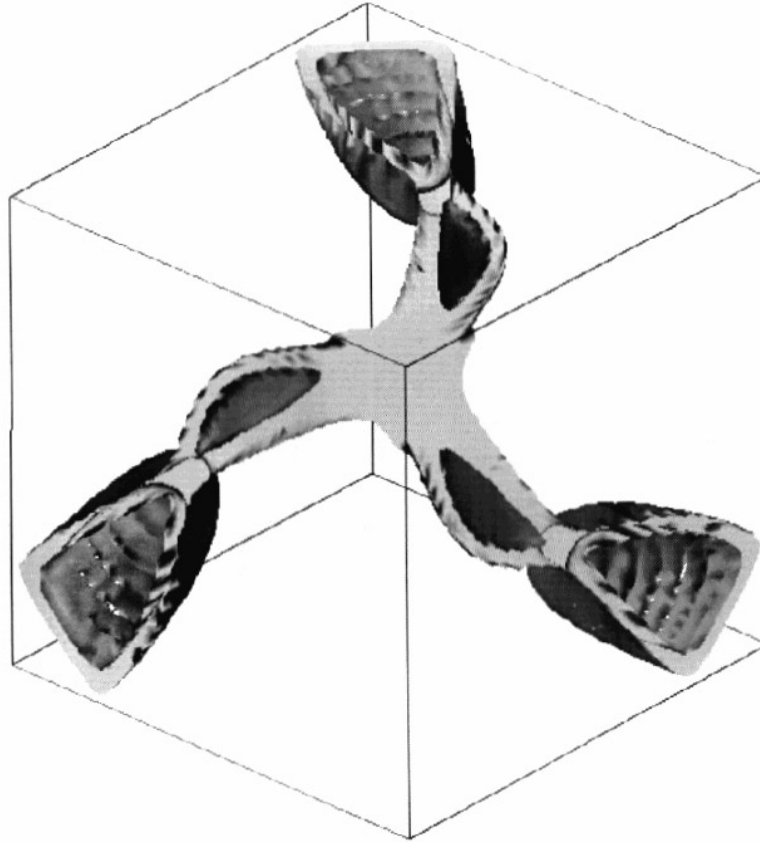


Figure 3. (a) [100] and [111] sections of reciprocal space of ZrW_2O_8 showing loci of the wave vectors where RUMs exist. (b) A three-dimensional surface of the RUM wave vectors in an octant of the Brillouin zone of ZrW_2O_8 . The origin of reciprocal space is to the fore.



(b)

Figure 3. Continued.

(translational) form as the wave vector moves away from $k = 0$, with a rapidly increasing rotational contribution.

The same approach also gives the QRUMs as very low-frequency solutions of the same dynamical matrix. Although the distinction between QRUMs and all other vibrations might be arbitrary, in practice some level of distinction can usually be made. The calculations showed the existence of four bands of QRUMs over the whole of reciprocal space, and that the exotic surface of RUMs discussed above actually lies within one of the bands of QRUMs.

3. Calculations with empirical model potentials

In order to validate our RUM interpretation of the negative thermal expansion in ZrW_2O_8 we have performed some model calculations using atomistic simulations based on the ionic model [12], noting that free-energy minimization techniques have previously predicted the negative thermal expansion of several zeolites ahead of experiment [13]. Our models have

used simple short-range potential energy functions of the form

$$\varphi(r) = B \exp(-r/\rho) - Cr^{-6}.$$

We used formal ionic charges, and a shell model for the oxygen anion. In this representation the charge on the anion was -2.84819 electron units. The core and shell interacted through a harmonic potential in the core-shell separation u :

$$\varphi(u) = \frac{1}{2}ku^2.$$

We used the value $k = 74.92 \text{ eV } \text{\AA}^{-2}$. The values for the shell model, and the parameters for the short-range O...O potentials, were taken from a good empirical model for SiO₂ [14] and were not adjusted at all. We also included a bond-bending potential of the form

$$\varphi(u) = \frac{1}{2}K(\theta - \theta_0)^2.$$

In one approach we used an existing potential for Zr...O taken from work on ZrO₂ [15], and found parameters for the W...O and O-W-O potentials which best reproduce the crystal structure. With the lack of any other experimental data for ZrW₂O₈ (such as elastic and dielectric constants, or phonon frequencies) it was not possible to define a unique set of parameters, but one set we have worked with gives reasonable values for a range of physical properties. In a second approach we first developed the W...O potential parameters by fitting to the CaWO₄ scheelite structure and vibrational frequencies [16]. We then fitted the Zr...O potential by optimizing against the calculated crystal structure. The parameters for the short-range potentials in this second approach are given in table 1. The values for the parameter K in the bond-bending potential were 0.4 and 0.5 eV for the O-Zr-O (equilibrium angle 90°) and O-W-O (equilibrium angle 109.47°) bonds respectively.

Table 1. Derived interatomic potentials for ZrW₂O₈. O-O interactions were taken from [14].

Ion pairs	B (eV)	ρ (Å)	C (eV Å ⁶)
W-O	1305.22	0.375	0.0
Zr-O	9000000	0.140	0.0
O-O	22764.0	0.149	27.879

The quality of the model potential can be assessed by comparing the calculated crystal structure with the experimental data. In table 2 we compare the cell parameters and the bond lengths. It can be seen that the maximum discrepancy is less than 2%. Although the elastic constants have not been measured, we have calculated the values $C_{11} = 2.37$ GPa, $C_{12} = 1.38$ GPa, and $C_{44} = 0.22$ GPa. These values fulfil the stability requirements of the cubic structure given by the elastic constants.

Table 2. Comparison of calculated and experimental crystal structures of ZrW₂O₈.

	Observed [1]	Calculated
Cell parameter (Å)	9.160	9.099
Zr-O (Å)	3 × 2.042, 3 × 2.109	3 × 2.093, 3 × 2.118
W1-O (Å)	1.707, 3 × 1.798	1.741, 3 × 1.769
W2-O (Å)	1.733, 3 × 1.782	1.721, 3 × 1.748

The thermal expansion can be calculated within the quasiharmonic approximation by relaxing the structure at constant pressure to minimize the total free energy (lattice potential

energy + phonon free energy). We performed calculations over the temperature range 5–350 K (the reported stability range of the ordered structure of ZrW_2O_8), and obtained a value for the thermal expansion coefficients of $-9.4 \times 10^{-6} \text{ K}^{-1}$. This agrees remarkably well with the value of $-9.5 \times 10^{-6} \text{ K}^{-1}$ extracted from the data plotted in [1]. Whilst the extremely close agreement may be fortuitous to some extent, rather than an exact reflection of the quality of our potential model, we nevertheless believe that, if our RUM interpretation of the negative thermal expansion is correct, it is likely that any reasonable potential model will give a good calculation of the negative thermal expansion. Indeed, the first model also gave reasonably good results. To obtain more information, we calculated the mode Grüneisen parameters [12] for a number of wave vectors. Our results showed that the QRUMs are contributing as effectively to the negative thermal expansion as the RUMs. In both cases, the significant rotational components and the low frequencies operate together.

4. The rigidity of the WO_4 tetrahedra and ZrO_6 octahedra

The RUM model requires that we can actually think of the WO_4 tetrahedra and ZrO_6 octahedra as being rigid on the relative energy scale of all other deformations of the ZrW_2O_8 structure. The question of the actual rigidity of the WO_4 tetrahedra and ZrO_6 octahedra is best tackled by considering the frequencies of vibrational modes that involve distortions of these units. The important modes for this purpose are those that involve bending of the O–W–O and O–Zr–O bond angles, rather than the higher-energy W–O and Zr–O stretch modes. The internal vibrational modes of the WO_4 tetrahedra have been measured for the mineral scheelite, $CaWO_4$. The frequencies of the bond-bending modes are 10–13 THz [16], which should be compared with the values of 13–20 THz for the SiO_4 tetrahedra in Mg_2SiO_4 [17]. To determine the stiffness of the ZrO_6 octahedra we have considered the cubic perovskite $BaZrO_3$, in which they are corner linked. The $k = 0$ transverse optic phonons were calculated from first principles using density functional theory, with pseudopotentials, in the local density approximation. The frequencies of the modes involving deformation of the ZrO_6 octahedra were calculated as 3.4, 5.5 and 18.0 THz (the other modes are the transverse acoustic mode and the ferroelectric mode involving the displacement of the Ba cation). The highest-frequency mode mostly involves Zr–O stretching motions. These frequencies should be compared with the values of 5.2, 13.4 and 26.3 THz calculated for the SiO_6 modes in $MgSiO_3$ perovskite [18]. These comparisons show that the WO_4 tetrahedra are probably about half as stiff as SiO_4 tetrahedra, and the ZrO_6 octahedra are rather less stiff in comparison with the SiO_6 octahedra, but nevertheless the forces for distorting these units are high compared to the forces involved when neighbouring units rotate against each other.

5. The phase transition at 430 K in ZrW_2O_8

We now consider the issue of the phase transition at 430 K in ZrW_2O_8 . Perhaps surprisingly, this does not have a large effect on the thermal expansion [1]. Mary *et al* [1] proposed two possible interpretations of the disordered high-temperature phase. In the first there is some orientational disorder of the WO_4 tetrahedra. This is quite possible since one of the W–O bonds is non-bridging, so a single tetrahedron can be reflected through the plane of the three bridging oxygens. However, the neighbouring WO_4 tetrahedra along [111] and related directions will have to undergo correlated reorientations in order to avoid an unacceptably close O...O distance.

It is not possible to perform our RUM analysis on this disordered structure, but the important thing is that the precise orientation of the WO_4 tetrahedra will not affect the topology of the structure. In particular the local structure with pairs of WO_4 tetrahedra being reflected together will hardly change at all. We therefore envisage that the RUM spectrum will be only slightly affected, and the mechanism for the negative thermal expansion will remain.

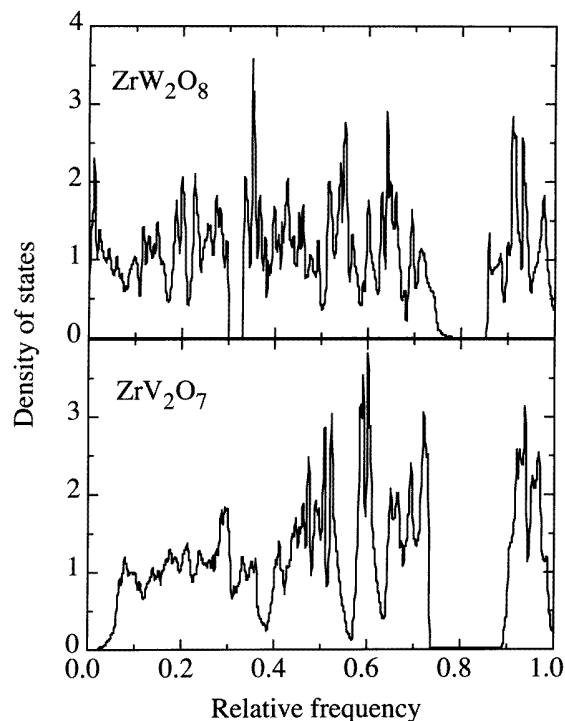


Figure 4. The vibrational density of states for ZrW_2O_8 and ZrV_2O_7 calculated using our split-atom method [6, 9, 11], showing that there are many more low-frequency modes in ZrW_2O_8 than in ZrV_2O_7 . It can be seen that the density of states in ZrV_2O_7 follows a normal Debye parabolic form at low frequencies, whereas the density of states in ZrW_2O_8 has a continuum of states over the same low-energy range, which arise from the RUMs and QRUMs present in this structure.

The second possible structure of the high-temperature phase proposed by Mary *et al* [1] involved the formation of W_2O_7 and W_2O_9 groups. These complexes will provide some cross-bracing of the framework of linked rigid units, which will have a significant effect on the existence of the RUMs. Whilst we cannot model this type of disorder, we can instead consider the crystal structure of ZrV_2O_7 (figure 1), which is structurally similar with the cross-bracing arising from the V_2O_7 linkages. Our RUM calculations for this material show that there are no RUMs at all in this structure, and no elastic flexibility. This point is highlighted in figure 4, which shows the vibrational density of states (plotted on a relative scale) for both ZrW_2O_8 and ZrV_2O_7 calculated using the split-atom method described above [6, 9, 11]. Whilst there are many similarities between the two materials in the vibrational density of states over a wide energy range, it is clear that there are many more low-energy modes in ZrW_2O_8 than in ZrV_2O_7 , at least within the harmonic approximation,

as seen in the increased level of the vibrational density of states at frequencies below 0.08 on the relative scale. The vibrational density of states of ZrV_2O_7 shows a normal Debye dependence ($g(\omega) \propto \omega^2$) at low frequencies, whereas in ZrW_2O_8 there is almost a continuum of low-frequency modes at low frequencies. These low-energy modes are the RUMs and QRUMs we have considered above, which are clearly of much less significance in the ZrV_2O_7 structure. This comparison suggests that the additional cross-bracing of the structure adds a significant degree of rigidity to the structure, and if the high-temperature phase of ZrW_2O_8 contains such cross-bracing it is quite likely that the thermal expansion of the two phases will be rather different.

We should note, however, that the changes in structure that occur at the phase transition are quite large compared to the changes that occur at many structural phase transitions. In effect they involve rebuilding the WO_4 tetrahedra, which will be a high-energy process. This suggests that the actual reorientation rate will be very slow. At the temperature of the phase transition it is not likely that the WO_4 tetrahedra will lose their rigidity.

6. Negative thermal expansion in ZrV_2O_7

Korthuis *et al* [5] attributed the negative thermal expansion in ZrV_2O_7 to the behaviour of the V–O–V bonds. The space-group symmetry gives an average structure that implies an average bond angle of 180° , but it is likely that this corresponds to a high-energy configuration. Thus any two linked VO_4 tetrahedra would actually like to rotate relative to each other in order to reduce the V–O–V angle. This is very like the situation in β -cristobalite [7–9, 19–21], where the average crystal structure suggests linear Si–O–Si bonds, but on a local scale the SiO_4 tetrahedra can rotate to give Si–O–Si angles of around 145° . In this case there are many RUMs available to allow the tetrahedra to rotate away from their ‘average’ orientations without having to distort. In ZrV_2O_7 there are no RUMs, so any rotations of the VO_4 tetrahedra will cause the ZrO_6 octahedra to distort, giving a balance between the stiffness of the octahedra and the energy gain in bending the V–O–V bonds. The rotations of the VO_4 tetrahedra will necessarily pull the rest of the structure in, giving a volume reduction [5]. Since these rotations, and hence volume reduction, will be larger at higher temperatures, there will be a negative thermal expansion. This effect will be smaller if the tetrahedra are smaller, which accounts for the observation that the P-rich members of the ZrP_2O_7 – ZrV_2O_7 series have positive thermal expansion [5].

7. Conclusion

In conclusion, we propose that the existence of low-frequency RUMs with wave vectors on complicated three-dimensional surfaces in reciprocal space may provide a mechanism for the negative thermal expansion observed over a wide range of temperatures in ZrW_2O_8 . This explanation accounts naturally for the weak effect of the phase transition at 430 K on the negative thermal expansion. We also propose that the mechanism for the negative thermal expansion in ZrV_2O_7 is qualitatively different.

The important point is that, although both ZrW_2O_8 and ZrV_2O_7 have negative thermal expansion, the fact that the suggested mechanism for the effect in ZrV_2O_7 is not relevant for ZrW_2O_8 implies that the mechanism in ZrW_2O_8 is qualitatively different, although both will involve the volume reduction induced by rotating polyhedra. In the case of ZrW_2O_8 it is much more likely that it is the greater flexibility of the structure, as evidenced by our RUM calculations, that is the crucial factor.

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