

LETTER TO THE EDITOR

Symmetric Stretching Vibrations of Two-Coordinate Oxygen Bridges as a Cause for Negative Thermal Expansion in $ZrV_xP_{2-x}O_7$ and AW_2O_8 ($A = Zr, Hf$) at High Temperature

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To examine the origin of negative thermal expansion in oxides $ZrV_xP_{2-x}O_7$ ($x = 0-2$) and AW_2O_8 ($A = Zr, Hf$), *ab initio* self-consistent-field molecular orbital calculations were carried out for a model compound $(HO)_3P-O-P(OH)_3^{2+}$. Our study suggests that symmetric stretching vibrations of two-coordinate oxygen bridges are strongly coupled with their bending vibrations and are more important for negative thermal expansion at high temperature. The oxygen bridges accommodate a large stretching of the $A-O$ ($A = Zr, Hf$) and $M-O$ ($M = P, V$) bonds at high temperature by decreasing the bond angles of the oxygen bridges. When the bond angles increase, the bonds are shortened due to the π -type orbital interactions associated with the oxygen lone pair orbitals. © 1997 Academic Press

INTRODUCTION

Recently, Sleight and co-workers prepared several transition metal oxides that exhibit negative thermal expansion (1–6). For example, the thermal expansion of cubic $ZrV_xP_{2-x}O_7$ ($x = 0-2$) can be very small and even negative as x increases (Fig. 1) (1). Cubic ZrM_2O_7 ($M = V, P$) phases have the NaCl structure with Zr^{4+} and $M_2O_7^{4-}$ as the cation and anion, respectively (1, 3). Each Zr is surrounded with six M_2O_7 units to form a ZrO_6 octahedron, so the oxygen atoms are two-coordinate bridging atoms of the $Zr-O-M$ and $M-O-M$ linkages. The crystal structure of ZrP_2O_7 at room temperature shows that the thermal ellipsoids of the oxygen atoms are large primarily perpendicular to the $P-O-P$ and $Zr-O-P$ bridges, and hence there is a large uncertainty in the $P-O-P$ and $Zr-O-P$ bond angles. The lattice symmetry of the high-temperature (above $\sim 290^\circ\text{C}$) structure for ZrP_2O_7 forces the $P-O-P$ linkage to be linear on average (3). However, this may be a consequence of thermal motion or disordered arrangements of bent $P-O-P$ linkages.

To explain the low and negative thermal expansion in cubic ZrM_2O_7 at high temperature, Sleight and co-workers proposed the bending vibration model in which transverse bending vibrations in the $M-O-M$ linkages is considered to shorten the $M\cdots M$ distances (**1a**) (1–5) (see Scheme 1). This model assumes that the $M-O$ bond lengths remain nearly unchanged in bending vibrations, so negative thermal expansion is easily predicted when the $M-O-M$ linkage is linear at low temperature. However, the normal $M-O-M$ bond angle is not 180° (e.g., $130^\circ-160^\circ$ for $M = P$) (7). In addition, negative thermal expansion occurs in AW_2O_8 ($A = Zr, Hf$) (4–6), in which each WO_4 tetrahedron shares three of its four oxygen atoms with adjacent AO_6 octahedra, although their $A-O-W$ linkages are all bent (e.g., $\angle Zr-O-W = 154.3^\circ, 171.8^\circ$ at room temperature) (4). Since the bending vibration model assumes rigid $M-O$ bonds, the thermal ellipsoid of M is expected to be elongated along the direction of linear $M-O-M$ linkage (**1a**, **1b**). However, the reported thermal ellipsoid (though isotropic) of M is small (3), so that during bending vibrations the position of the M atom does not appear to change (**1c**). This is possible only if the $M-O$ bond length decreases as the $M-O-M$ bond angle increases. At high temperatures (e.g., over $\sim 290^\circ\text{C}$), thermal energies are high enough to cause extensive vibrational excitations involving $M-O$ stretching vibrations. Consequently, $M-O-M$ bending vibrations are expected to be strongly coupled with $M-O$ bond symmetric stretching vibrations. To probe these questions, we carried out *ab initio* self-consistent-field molecular orbital (SCF-MO) calculations for a model compound, $(HO)_3P-O-P(OH)_3^{2+}$ (**2**), hydrogen terminated pyrophosphate ion (see Scheme 2).

RESULTS OF CALCULATIONS

Our SCF-MO calculations for **2** were performed using the Gaussian-92 package with a 6-31G* basis set (8).

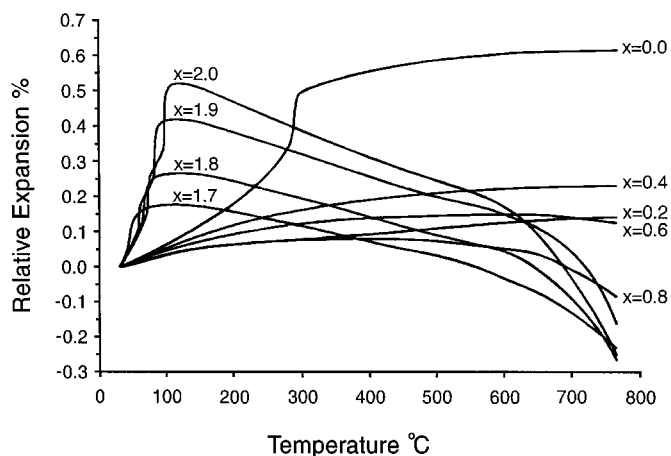
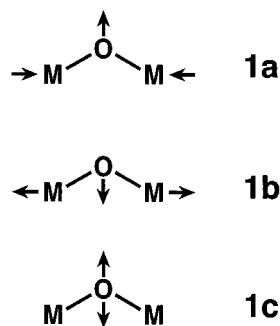
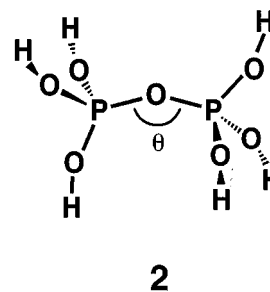


FIG. 1. Relative expansion of the unit cell of $ZrV_xP_{2-x}O_7$ as a function of temperature (adapted from Fig. 2 of Ref. 1).

For convenience, we represent the bridging oxygen atom of the P–O–P linkage by O_B and the remaining oxygen atoms of **2** by O_T 's ("terminal" oxygen atoms). The H– O_T bond length was fixed at 0.96 Å and the P– O_T –H bond angle at 170.7° (i.e., the P– O_T –Zr bond angle of ZrP_2O_7). Complete optimization of the remaining geometrical parameters for **2** shows that P– O_B = 1.574 Å, P– O_T = 1.481 Å, $\angle O_B$ –P– O_T = 108.9°, and $\angle P$ – O_B –P = 159.4°. Thus the P–O–P linkage is predicted to be bent, in good agreement with experiment (6). When the P– O_B –P bond angle is optimized as a function of the P– O_B bond length, the optimum bond angle θ_{opt} , is found to gradually approach 180° as the P– O_B bond length is reduced (Fig. 2). This trend is in good agreement with experiment (7). Consequently, as the P– O_B bond length increases, the P...P distance increases more slowly (e.g., within the range of the P– O_B bond lengths studied in our calculations, ~8% increase in the P– O_B bond length induces ~2.5% increase in the P...P distance). The electronic factor leading to the M–O bond shortening is the π -type orbital interactions of the oxygen lone pair orbitals with the acceptor π^* orbitals of the MO_4



SCHEME 1



SCHEME 2

groups (**3a** for P_2O_7 and **3b** for V_2O_7) (9) (see Scheme 3). These stabilizing interactions become stronger, and hence the M–O bond length becomes shorter, as the M–O–M bond angle approaches 180°. Thus, during P– O_B –P bending vibrations, the P– O_B bond length cannot remain constant but becomes shorter as the P– O_B –P bond angle approaches 180°. Therefore, P– O_B bond symmetric stretching vibrations should be strongly coupled with P– O_B –P bending vibrations (10).

Our results for **2** are essentially the same in nature as those found for the disiloxo unit $(HO)_3Si-O-Si(OH)_3$ (11, 12): the Si–O–Si linkage is bent, and the Si–O bond length decreases as the Si–O–Si bond angle approaches 180°. The latter has been explained in terms of the π -type orbital interactions of the oxygen lone pair orbital with the acceptor π^* orbitals of the SiO_4 groups (11, 12).

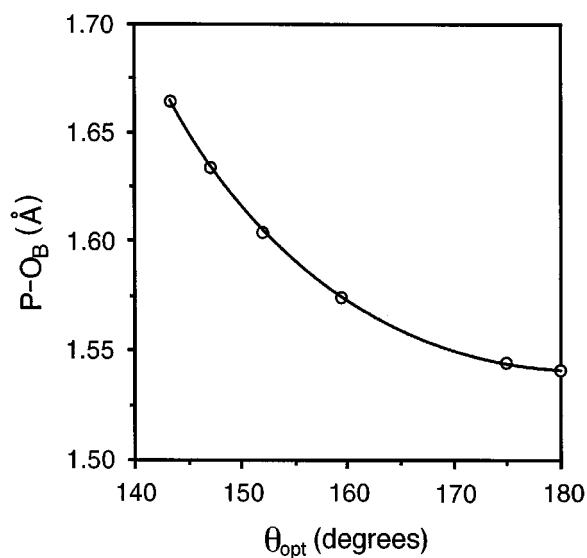
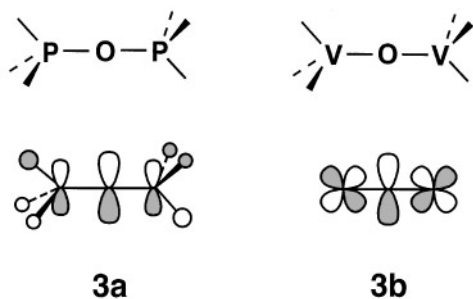


FIG. 2. Optimum P– O_B –P bond angle, θ_{opt} , of **2** calculated as function of the P– O_B bond length.



SCHEME 3

DISCUSSION

At high temperatures it is reasonable to assume that there occur extensive vibrational excitations involving Zr–O and M–O bond stretching in ZrM_2O_7 , thereby increasing the equilibrium Zr–O and M–O bond lengths. Thus, small or negative thermal expansion at high temperature should be considered as a consequence of accommodating increased bonds and their symmetric stretching vibrations confined in the Zr–O–M and M–O–M linkages. At high temperatures, the vibrationally stretched Zr–O and M–O bonds are longer than their equilibrium bond lengths, and simultaneous stretching of two bonds in the Zr–O–M and M–O–M linkages is facilitated if the Zr...M and M...M distances are decreased. This is reasonable because the potential well for bending is much softer than that for stretching. When the bonds contract vibrationally so that the Zr–O–M and M–O–M bond angles increase, the π -type orbital interactions involving the oxygen lone pair orbitals become enhanced and shorten the bonds, which has the effect of preventing the Zr...M and M...M distances from increasing. This symmetric stretching vibration model is more favorable if the equilibrium geometries of the two-coordinate oxygen bridges are bent.

The symmetric stretching vibration model is consistent with the observation for ZrP_2O_7 that the oxygen atoms of not only the P–O–P but also of the Zr–O–P linkages have large thermal ellipsoids perpendicular to the bonds (3). The π -type orbital interactions involving the oxygen lone pair orbital are expected to be stronger with the empty d -block orbitals of the ZrO_6 octahedron and VO_4 tetrahedron than with the π^* -type group orbitals of the PO_4 tetrahedron (9). Thus, the bond shortening effect in the M–O–M and Zr–O–M linkages would be stronger for $M = V$ than for $M = P$. This explains why in $ZrV_xP_{2-x}O_7$ the tendency for negative thermal expansion increases with increasing x (Fig. 1). In a similar manner, the negative thermal expansion of AW_2O_8 ($A = Zr, Hf$) at high temperature can be explained in terms of the symmetric stretching vibrations of the A–O–W ($A = Zr, Hf$) bridges. This is consistent with the finding that the thermal ellipsoids of the bridging

oxygen atoms in ZrW_2O_8 are larger perpendicular to the bonds (4, 5).

The symmetric stretching vibration model is the same as the bending vibration model of Sleight and co-workers in that vibrations involving two-coordinate oxygen bridges are considered essential for negative thermal expansion. As already mentioned, the bending vibrations should be strongly coupled with symmetric stretching vibrations, and the equilibrium bond lengths should decrease as the bond angle increases toward 180° . Nevertheless, the major character of these coupled vibrations would be bending at low temperature, but symmetric stretching at high temperature. AW_2O_8 ($A = Zr, Hf$) systems are remarkable in that they exhibit negative thermal expansion from 0.3 K up to their decomposition temperatures of approximately 1050 K (4, 5). It is reasonable to explain the negative thermal expansion of these compounds in terms of the bending vibrations at low temperature and in terms of the symmetric stretching vibrations at high temperature.

CONCLUDING REMARKS

In the symmetric stretching vibration model, negative thermal expansion at high temperature is viewed as a way of accommodating increased bond stretching. This model suggests that small or negative thermal expansion at high temperatures occurs in oxides made up of two-coordinate oxygen bent-bridges when the following two conditions are met: (a) the oxygen atoms are linked to groups possessing low-lying π -type acceptor orbitals so that bond shortening effect is enhanced when the bond angle of the oxygen atom bridges increases, and (b) there is enough room around the oxygen atoms so that the oxygen bridges can undergo significant symmetric bond stretching vibrations.

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