Negative thermal expansion and its relation to high pressures

S K Sikka

Office of the Principal Scientific Adviser to the Government of India, 324-A,
Vigyan Bhawan Annexe, Maulana Azad Road, New Delhi 110011, India

Abstract

Most materials expand when heated. However, many exceptions are now known. Recently, interest in this has been revived with the discovery of isotropic negative thermal expansion (NTE) in ZrW_2O_8. From equation of state considerations, one can relate NTE to negative Grüneisen parameters (thermal or electronic). Under pressure, these lead to equation of state anomalies with the pressure derivative of the bulk modules being small or negative. Many of these materials undergo pressure-induced amorphization. This in some of them can be understood on the steric constraint model. It is also argued that NTE in most materials may be understood from the fact that these materials have two degenerate or nearly degenerate energy states. On increase of temperature, the material then samples the lower volume state, leading to NTE.

1. Introduction

The property of negative thermal expansion (NTE) of some materials has been known for a long time. However, it is only after the discovery of NTE in ZrW_2O_8 over a large temperature range [1] that an enormous interest has been generated. The structure of ZrW_2O_8 contains a network of corner sharing ZrO_6 octahedral and WO_4 tetrahedral units in an open framework. In this all the oxygens except one of MoO_4 are two-fold coordinated and the negative thermal expansion is attributed to the transverse anharmonic vibrations of the oxygen atoms [2]. NTE has since been discovered in other corner sharing polyhedral compounds of MO_2, AMO_5 and $A_2M_3O_{12}$ types ([3] and references therein).

As in NTE, the increase of temperature leads to compression and as it has been further related to the negative Grüneisen parameter [4, 5], it is natural to study these materials under pressure. Negative gamma leads to interesting anomalies in equation of state data. Surprisingly, most NTE materials show pressure-induced amorphization (PIA). Table 1 lists these substances. These results have led many authors to speculate that there is some correlation between NTE and PIA. In this paper, we dwell on these issues.

Table 1. List of framework compounds showing PIA.

Compound	Transition pressure (GPa)	Reference
ZrW_2O_8	1.5	[6]
HfW_2O_8	2	[7]
ZrV_2O_7	4	[8]
$ZrMO_2O_8$	8	[9]
$Sc_2(WO_4)_3$	4	[10]
$Lu_2(WO_4)_3$	7	[11]
$Al_2(WO_4)_3$	10	[12]
$Gd_2(MoO_4)_3$	6	[13, 14]
$Sm_2(MoO_4)_3$	6	[14]
$Eu_2(MoO_4)_3$	7	[14]

2. NTE and the equation of state

The pressure–volume relation of a condensed system may be written as (see Sikka *et al* [15] and references therein)

$$p = p_c(V) + \frac{\gamma 3k_B T + 1}{V} \frac{\gamma_e}{2} \frac{\beta T^2}{V}.$$

Here, p_c is the 0 K cold pressure. The second term is the contribution due to lattice vibrations and the third term is from thermal electronic excitations at temperature T. γ and γ_e are the lattice and electronic Grüneisen parameters and β is the electronic specific heat. It is obvious from the above expression that NTE can arise in the materials if they have:

  (i) a negative γ;
 (ii) a temperature dependent γ [16]; and
(iii) a negative γ_e and a very large β as in case of heavy fermions [17].

Further, the lattice γ may be related to p_c and to the pressure derivative of the bulk modulus (B')

$$\gamma(V) = \frac{t-2}{3} - \frac{V}{2} \left(\frac{d^2 p_c V^{2t/3}}{d^2 V} \right) \left(\frac{d p_c V^{2t/3}}{dV} \right)^{-1}$$

and

$$\gamma = \frac{-t+1}{6} + \frac{1}{2}[B']_T.$$

Here $t = 0, 1$ and 2 correspond to Slater, Dugdale–Macdonald and free volume approximations. It is again clear that negative γ implies small or negative B' and a softer equation of state. This is experimentally observed in NTE materials. The $p-V$ (300 K) isotherms in ZrW_2O_8 and $ZrMo_2O_8$ are found to be linear. A computation of B' from the first principles total energy calculations for α-ZrW_2O_8 of Quyang *et al* [18] gives $B' = 1.15$. Mukherjee *et al* [19] obtained a decrease of compressibility with pressure in $Al_2W_3O_{12}$ with a corresponding cusp in the $p-V$ curve (figure 1). A similar result has been found recently in FeNi alloys [20] and Zn [21] at 7.5 and 10 GPa, respectively. These have been correlated with very small or negative thermal expansion by experiments at these pressures. More such observations will be found under pressure as γ is intrinsically related to p_c.
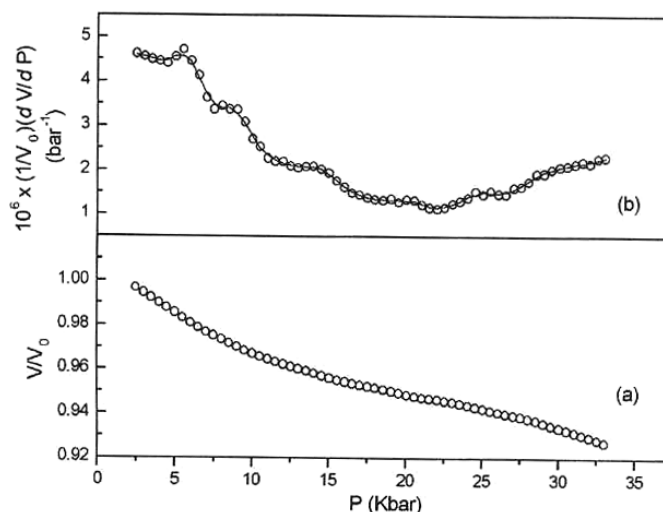
Figure 1. (a) $p-V$ data and (b) compressibility as a function of pressure for $Al_2W_3O_{12}$ (from [19]).
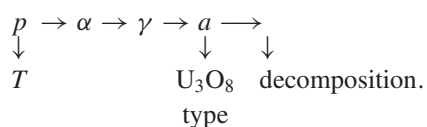
3. The mechanism of PIA for NTE structures

Sharma and Sikka [22] reviewed the data on PIA up to 1996 and the following rules were given for crystal to amorphous (c–a) phase changes.

(1) The pressure-induced amorphous state is a kinetically preferred one. It arises from the frustration of the parent metastable crystalline phase in transforming to the high-pressure equilibrium state due to the requirement of thermal energy to overcome the energy barrier. The c–a transition under pressure then follows a three-level free energy diagram (figure 2).

(2) The equilibrium phase is usually of higher coordination or is dissociated.

(3) The structural frustration arises as, for example while achieving higher coordination, some of the non-bonded distances become too short and make a repulsive contribution to the free energy. Further compression results in the loss of long-range order by taking advantage of the enhanced entropy.

(a) ZrW_2O_8

The equilibrium phase here is the dissociated one (1): $ZrW_2O_8 \rightarrow ZrO_2 + WO_2$ and α-ZrW_2O_8 and γ-ZrW_2O_8 (phase above 0.21 GPa) are metastable phases. Grzechnik *et al* [23] have determined some portion of the temperature–pressure phase diagram. It is schematically depicted below:

$$p \rightarrow \alpha \rightarrow \gamma \rightarrow a \longrightarrow$$
$$\downarrow \qquad\qquad\quad \downarrow \qquad \downarrow$$
$$T \qquad\qquad\quad U_3O_8 \quad \text{decomposition.}$$
$$\text{type}$$

In the U_3O_8 form, the W atom in ZrW_2O_8 is six-coordinated with oxygen atoms. It is obvious that this system follows the three-level free energy diagram. In both crystalline phases, Mo tetrahedra are on the verge of a coordination change (figures 3(a) and (b)). In α-ZrW_2O_8, the W2-coordinated O3 atom has a very short (2.41 Å) contact with W1 and the
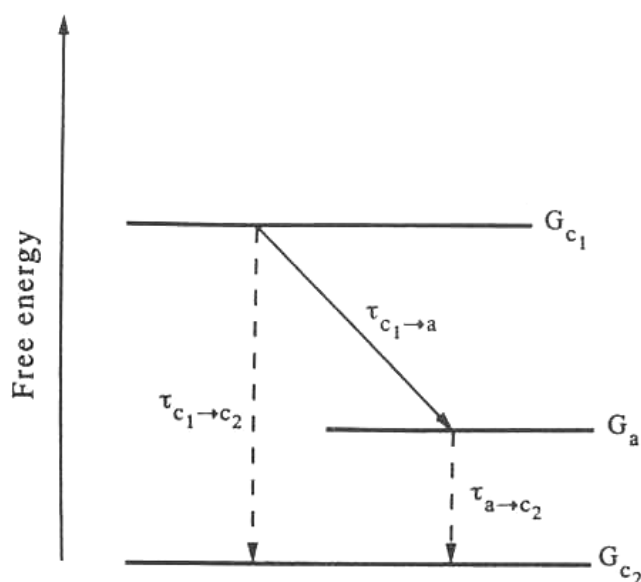
Figure 2. A three-level free energy diagram for c–a transformations. G_{c_1}, G_a and G_{c_2} are the free energies for the metastable crystalline (c_1), amorphous (a) and equilibrium phases (c_2). The τ represent relaxation times with $\tau_{c_1-c_2} > \tau_{c_1-a}$ and $\tau_{c_1-a} < \tau_{a-c_2}$.

O3–O1 distance is 2.7 Å. This is almost of the same value in SiO_2 and $AlPO_4$ just prior to their amorphization under non-hydrostatic pressures [24]. Further compression would result in a repulsive contribution to the total energy and the structure would be sterically constrained. To relieve this, the α-phase first transforms to the γ-phase. In this the bonding situation around the same W atoms is depicted in figure 3(b). The angle W1–O3–W2 is bent ($142°$ compared to $180°$ in the α phase). The polyhedra are also more distorted. This is again very similar to SiO_2 [25]. To achieve a proper W1–O3 bond length (-1.9 Å), a thermal activation will be required. Further compression without it destabilizes the lattice structure with consequent PIA.

(b) $ZrMo_2O_8$

The ambient trigonal α-$ZrMo_2O_8$ is again a metastable phase and the equilibrium phase is monoclinic ($C2/c$) β-$ZrMo_2O_8$ [26]. In the latter, the Mo polyhedra are distorted octahedra and Zr polyhedra ZrO_8 units. α-phase transforms to γ-$ZrMo_2O_8$ ($C2/m$) at about 1 GPa and further to ϵ-$ZrMo_2O_8$ (triclinic) at 2.5 GPa before amorphization near 8 GPa [9]. The γ-phase has the same topology as the parent structure and with the type of relation of cell parameters between the monoclinic and triclinic lattices, it is also not expected to change in the triclinic phase. So, for the present purposes we consider the bonding environment of Mo atoms in the trigonal phase, which is shown in figure 4. A distance least squares (DLS) [27] refinement for higher compression shows that without thermal activation, the steric constraints will be encountered. This is very near the experimental c–a transition point.

V/V_0	O2–O4 (Å)
1.0	3.13
0.95	2.70
0.90	2.64

(a)

O_3---O_1=2.70 Å
O_3---O_2=2.85

(b)

O_3---O_1=2.65 Å
O_3---O_2=2.95

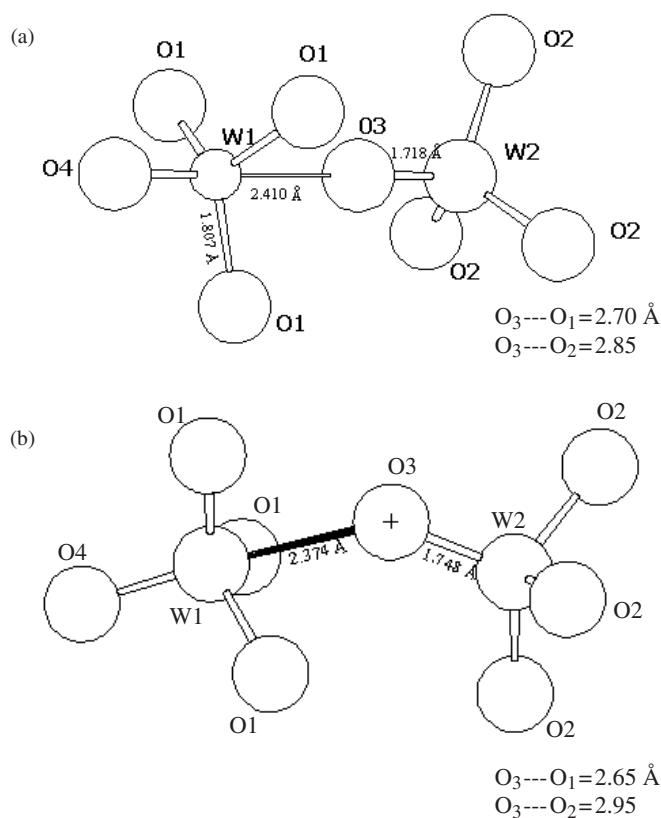**Figure 3.** The structural arrangement of WO_4 groups in (a) α-ZrW_2O_8 and (b) γ-ZrW_2O_8. Here atoms have the same symbols as in (a).

(c) $A_2M_3O_{12}$ compounds

A greater number of compounds in this class have been investigated. In fact the field of PIA owes it origin to the study of $Gd_2Mo_3O_{12}$ by Brixner in 1972 [13]. In $Al_2W_3O_{12}$, a decomposition reaction has been observed at 1.5 GPa and 900 °C [28]. These compounds at ambient conditions contain AO_6 octahedra and MO_4 tetrahedra in which each vertex is shared and each oxygen is two-coordinated. Due to the complexity of this arrangement the compression mechanism for NTE involves polyhedral tilting. Although individual A–O–M angles show both positive and negative changes, the average value of these angles decreases with decrease in volume of the unit cell [29]. Again, we have done DLS refinements as a function of compression for $Sc_2W_3O_{12}$, employing the measured cell parameters by Sharma *et al* [30]. The structural model for PIA similar to cases (a) and (b) above is indicated. Additionally, the polyhedra also distorted. Steric constraints are encountered very near experimental PIA transition pressures.

4. Discussion

It is clear from the above that the amorphization that occurs in some of the corner-linked framework structures is not from the parent phase but from a high-pressure phase. A negative thermal expansion property is not established in many of these structures. For example, in
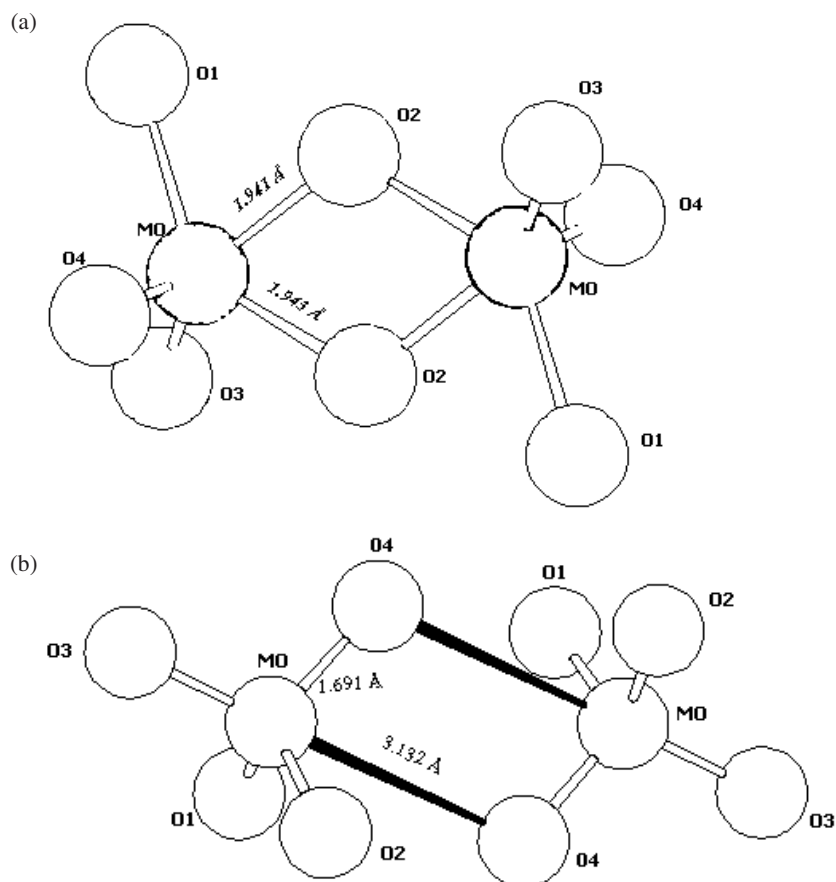
(a)

(b)

Figure 4. The structural arrangement of MoO_4 groups in (a) α-$ZrMo_2O_8$ and (b) β-$ZrMo_2O_8$.

ZrV_2O_7, PIA occurs from the $3 \times 3 \times 3$ supercell via a phase transition [8] where it shows a positive thermal expansion from very low temperatures up to about $100\,°C$ [31]. So in a corner sharing structure, is the occurrence of PIA and NTE correlated? The answer to this question will need further high-pressure–high-temperature work similar to that in FeNi alloys [20].

For metallic substances having NTE, a two-state or ground state degeneracy models have been proposed. In this the volume of one of the states is smaller, and so the fluctuations due to temperature that sample the lower volume state will lead to NTE. This has been invoked in invar where the two states are itinerant magnetic and non-magnetic ones. The latter is contracted [32]. Similarly, in δ-Pu the fluctuations between the fcc and the bcc phases may be responsible for NTE. Electronic structure calculations give a low barrier Bain path between the fcc and the lower volume bcc structures here [33]. What about the oxide framework compounds? Jorgensen *et al* [2] already give a hint for this in ZrW_2O_8. As pointed out above, these compounds are in metastable states at ambient conditions, and their equilibrium phases are of lower volume. These latter are accessible on heating. The fluctuations on increase of temperature that sample the lower volume phase may then lead to NTE, provided the energy barriers are low. Detailed energy barrier computations are needed to verify this hypothesis.

Acknowledgments

References

[1] Mary T A *et al* 1996 *Science* **272** 90
[2] Jorgensen J D *et al* 1999 *Phys. Rev.* B **59** 215
[3] Tao J Z and Sleight A W 2004 *J. Solid State Chem.* at press
[4] Mittal R *et al* 2001 *Phys. Rev. Lett.* **86** 4692
[5] Ravindran T R, Arora A K and Mary T A 2000 *Phys. Rev. Lett.* **84** 3879
[6] Perottani C A and da Jornada J A H 1998 *Science* **280** 886
[7] Parise J B *et al*, unpublished
[8] Carlson S and Andersen A M K 2001 *J. Appl. Crystallogr.* **34** 7
[9] Carlson S and Andersen A M K 2000 *Phys. Rev.* B **61** 11209
[10] Secco R A *et al* 2002 *J. Phys. Chem. Solids* **63** 425
[11] Liu H *et al* 2002 *Solid State Commun.* **121** 177
[12] Garg N *et al* 2001 *Solid State Phys.* 39
[13] Brixner L H 1972 *Mater. Res. Bull.* **7** 879
[14] Dmitriev V *et al* 2003 *J. Phys. Chem. Solids* **64** 307
[15] Sikka S K, Godwal B K and Chidambaram R 1998 *High-Pressure Shock Compression of Solids* vol 3,
        ed L Davison and H Shahinpoor (New York: Springer) p 1
[16] McMahan A K, Skriver H L and Johansson B 1981 *Phys. Rev.* B **23** 5016
[17] Berdi C D *et al* 1984 *Phys. Rev. Lett.* **52** 1982
[18] Quyang L, Xu Y N and Ching W Y 2002 *Phys. Rev.* B **65** 113110
[19] Mukherjee G D *et al* 2003 *J. Phys. Chem. Solids* **64** 611
[20] Dubrovinsky L *et al* 2001 *Phys. Rev. Lett.* **86** 4851
[21] Takemura K *et al* 2001 *Phys. Rev.* B **65** 132107
[22] Sharma S M and Sikka S K 1996 *Prog. Mater. Sci.* **40** 1
[23] Grzechnik A *et al* 2001 *Chem. Mater.* **13** 4205
[24] Sikka S K and Sharma S M 1992 *Curr. Sci.* **63** 317
[25] Hazen R M *et al* 1989 *Solid State Commun.* **72** 507
[26] Achary S N *et al* 2002 *Phys. Rev.* B **66** 184106
[27] Barerlocher C, Hepp A and Meier W M 1977 Institute of Crystallography and Petrology, ETH, Switzerland
[28] Achary S N *et al* 2002 *J. Mater. Sci.*
[29] Evans J S O, Mary T A and Sleight A W 1998 *J. Solid State Chem.* **137** 148
[30] Sharma S M *et al* 2003 unpublished
[31] Khosrovani N, Sleight A W and Vogt T 1997 *J. Solid State Chem.* **132** 355
[32] Schilfgaarde M, Abrikosov I A and Johansson B 1999 *Nature* **400** 46
[33] Dai X *et al* 2003 *Science* **300** 953