of diamond, with NbO having the lowest compressibility of the group. Measurements of the compressibilities of the oxides are presented in the succeeding paper.

References


Compressibilities and Grüneisen Constants of the Monoxides of Titanium, Vanadium and Niobium

BY A. TAYLOR AND N. J. DOYLE

Westinghouse Research Laboratories, Pittsburgh, Pennsylvania 15235, U.S.A.

(Received 29 June 1970; accepted 16 November 1970)

The compressibilities of titanium, vanadium and niobium monoxide have been determined using an X-ray tetrahedral anvil press with NaCl as an internal standard. An extrapolation technique involving the plotting of \((\Delta a/a)_\text{NaCl} \) versus \((\Delta a/a)_\text{oxide} \) was developed for eliminating the errors in lattice parameter determination resulting from movement within the pressure cell. The Grüneisen constants of the monoxides were evaluated using published specific heat data and our own determinations of thermal expansion.

1. Introduction

In the preceding paper (Taylor & Doyle, 1971), details were given concerning the preparation and thermal expansion properties of the vacancy-containing NaCl-type monoxides \((\text{TiO})_{0.856}(\square)_{0.144}, (\text{VO})_{0.848}(\square)_{0.152}\) and \((\text{NbO})_{0.730}(\square)_{0.250}\), where \((\square)_x\) represents the vacancy fraction. It has also been shown that whereas the vacancy fraction \(x\) in \((\text{TiO})_{1-x}(\square)_x\) can be reduced to zero by compressing the monoxide in a tetrahedral anvil press at 77 kbar and 1650°C (Taylor & Doyle, 1970), only a relatively small amount of vacancy filling takes place in the corresponding vanadium monoxide, and virtually none in niobium monoxide, the last two results being in agreement with those of Banus & Reed (1970).

It would be anticipated that the compressibility of vacancy free titanium monoxide would be less than for the 'normal' monoxide for which the vacancy fraction is \(x=0.144\). Because the tetrahedral press (Hall, 1962; Barnett & Hall, 1964) used to prepare this material was designed for use with a high intensity rotating anode X-ray tube (Taylor, 1966) for the purpose of taking Debye–Scherrer patterns of powders under high pressure, the opportunity itself of studying the effects of vacancy-filling on the compressibility of...
titanium monoxide, and of comparing these values with the compressibilities of the monoxides of vanadium and niobium. The availability of data on the specific heats of these materials, together with the determinations of their thermal expansion coefficients, also made it possible to compute their Grüneisen constants.

2. Experimental

2-1. General layout of press and X-ray apparatus

The tetrahedral press (by the McCartney Manufacturing Co. of Baxter Springs, Kansas) has a total load capacity of \(3 \times 10^5\) kg on rams 20-3 cm in diameter. Using tungsten carbide anvils with an edge length of 0.635 cm it was possible to apply a load of approximately 120 kbar on the sample without causing the anvils to fracture. The relationship between the X-ray tube and the press essentially conforms to the B-geometry of Barnett & Hall (1964) except that in our case the press stands in an ‘inverted’ position on one of its ram bases which fits into a cylindrical pedestal. Another difference is that, in our case, film is employed to record the diffraction spectra instead of a counter diffractometer.

Part of the experimental set-up is shown schematically in Fig. 1, where, for clarity, rams and tie-bars out of the plane of the diagram have been omitted. Because of the difficult geometry of the press, the high intensity rotating anode tube \(X\) was mounted on a double cross-slide fixture which was rigidly attached to the pedestal into which ram-base \(E_2\) was fitted. After passing through an adjustable collimator attached to the X-ray tube, the beam enters the press through the narrow gap between binding rings \(B_1\) and \(B_2\) and anvils \(A_1\) and \(A_2\) and, after traversing the tetrahedral cell \(T\) containing the sample to be X-rayed, the diffracted rays pass through the narrow gap presented by the second pair of binding rings and anvils (not shown) and impinge upon the film mounted in the cylindrical cassette \(H\). The cassette, which has a radius of 12.5 cm, is demountably attached to the adjustable support system \(G\) mounted on the steel tie-bar \(F_1\) which is 10 cm in diameter. The cassette is designed to accommodate diffraction lines on both sides of the direct beam up to 20 values of 50°, an angular range which is perfectly adequate for Ag and Rh \(K\alpha\) radiations and which is close to the maximum angle attainable through the edge of the tetrahedral cell. Means are provided to translate the cassette with uniform motion through a small, adjustable amplitude parallel to its cylindrical axis in order to widen and smooth out the diffraction pattern, should this be necessary.

2-2. Pressure cell and X-ray sample

The pressure cell, which is sketched in Fig. 2(a) is made in two symmetrical halves from a mixture consisting of 75% by weight of amorphous boron and 25% polypropylene (Prince & Okamoto, 1967). The X-ray sample is housed at the center in depressions approximately 0.012 cm deep in each half. In the first series of compressibility measurements, which were carried out on titanium monoxide at pressures up to 80 kbar, approximately, anvils were employed having an edge length of 1.27 cm along with pressure cells of edge length 1.91 cm. In extending the pressure range to about 120 kbar for all three monoxides, the anvil edge was reduced to 0.635 cm and cell edge to 1.27 cm. Finally, a few measurements were made on niobium monoxide up to about 100 kbar using an anvil edge length of 0.635 cm and an over-sized cell of edge 1.91 cm.

Upon compression, the cell extrudes out between the anvil flanks to form gaskets [Fig. 2(a)] which support part of the load. In the case of a cell of initial edge length 1.27 cm and a load of about 100 kbar on the sample, the breadth \([DJ, \text{ Fig. 2(a)}]\) of a gasket is about 0.4 to 0.5 cm, and its thickness 0.025 cm. The total path length for a diffracted ray through the cell and gaskets is about 2.0 cm. By actual measurements with a counter diffractometer, the linear absorption coefficient of the boron–polypropylene mixture was found to be \(\mu = 0.445\) for monochromatized Ag \(K\alpha\) radiation. Thus, in the absence of the X-ray sample, the effective beam strength is cut down by absorption in the cell to \(e^{-0.49}\) or 0.410 of its original intensity.

Because there can be no guarantee that the pressure in different cells of the same size would be the same for identical oil pressures in the press, and for reasons which will be presented later, it was decided not to employ the conventional phase-transition method of calibration by using the sudden resistivity changes which occur in metals such as Ti, Ba and Bi (Jeffery, Barnett, Vanfleett & Hall, 1966), but use instead a pressure scale based on the lattice compressibility of NaCl calculated by Decker (1965, 1968) with reference to a semi-empirical equation of state. To this end, the

Fig. 1. Plane section through X-ray tube, collimator system, film cassette and two hydraulic rams of tetrahedral anvil press. \(A_1A_2\) Tungsten Carbide anvils \(B_1B_2\) Binding rings \(C\) Guide rings \(D\) Rams \(E_1E_2\) Ram bases \(F_1F_2\) Tie bars \(G\) Film cassette support system \(H\) Film cassette (12.5 cm radius) \(T\) Tetrahedral cell \(X\) X-ray tube and collimator.
X-ray diffraction samples were made in the form of microfine powder mixtures of monoxide and NaCl in ratios which made the intensity of the 220 reflection of NaCl approximately equal to that of the closely adjacent 200 reflection from the monoxide, using Ag radiation. These mixtures were then compressed into flat discs suitable for producing transmission patterns. Tests were then carried out to determine the optimum thickness for highest transmission intensity. In the case of TiO and VO the best balance of intensities was obtained with a 1:1 weight ratio of NaCl to monoxide, and the optimum sample thickness \( t^* \) was approximately 0.050 cm. For NbO the NaCl to monoxide ratio was 2:1 and the optimum thickness \( t^* \) was 0.0225 cm. The measured value for \( \mu t^* \) was 1.03 and thus the intensity of the diffracted beam in the sample was reduced to \( e^{-1.03} \) or 0.357 of its initial value. Because the cell itself reduces the intensity by the factor 0.41, and the sample gives an additional factor of 0.357, the total reduction factor with Ag K\( \alpha \) radiation is 0.146. With Cu K\( \alpha \) radiated this factor would be less than 0.001.

### 2.3. Collimation

Choice of a suitable collimator for use in conjunction with the press represented, at best, a compromise between several conflicting factors. The best results were obtained with a tungsten carbide tube of length 7.5 cm, internal diameter 0.023 cm, and external diameter 0.125 cm, this latter dimension being of necessity small to enable the tube to fit in between the binding rings \( B_1B_2 \) as shown in Fig. 1. It would be expected that the intensity of the diffraction pattern would increase as the square of the beam diameter, with a concomitant decrease in the exposure time. This, however, is not the case. Partly on account of the cross rays, the effect of increasing the internal diameter of the tube is to spread the diffraction line over a wider angular range while simultaneously increasing the background level due to scattering from the cell at a faster rate. The net result is the production of a broadened line on a higher background, and thus a smaller signal-to-noise ratio. On the other hand, reducing the beam diameter to improve this ratio not only increases the exposure time but also reduces the number of crystals irradiated in the beam. This leads to the production of spotty diffraction lines, a condition which cannot be overcome as in conventional powder cameras by rotating or oscillating the sample.

In operating the press, there is an initial minimum oil pressure of about 4.2 kg.cm\(^{-2} \) on the rams which is required to close the anvils down on the pressure cell. This minimum pressure also serves to remove the initial slackness in the joints where the tie bars screw into the ram bases. This means that there is always a certain minimum pressure on the sample, the value of which depends on the cell size and also on whether one is at the initiation of the up-stroke or the termination of the down-stroke. With an anvil edge of 0.635 cm and a corresponding cell edge of 1.27 cm, some preliminary extrusion of the cell occurs and the resulting gasket is about 0.15 cm thick. The corresponding width of Debye–Scherrer pattern on the films is approximately 0.5 cm and the actual load on the sample will be about 9 kbar. With increasing pressure, the thickness of the gasket is reduced until, at about 150 kg.cm\(^{-2} \) oil pressure, corresponding to about 120 kbar on the sample, the thickness of the gasket is reduced to about 0.025 cm and the width of the Debye–Scherrer pattern to about 0.10 cm. At this stage it is sometimes advantageous to oscillate the X-ray film parallel to its cylindrical axis through an amplitude of about 0.1 cm to elongate the diffraction lines. This makes them easier to see and measure, but the exposure time must be correspondingly increased.

The anvil faces which effectively define the edges \( ADB \) and \( BIC \) of the tetrahedral cell [Fig. 2(a)] form, in effect, a pair of crossed slits beyond the tip of the col-

---

Fig. 2. Powder diffraction through tetrahedral cell (schematic). (a) cell geometry. (b) line displacement produced by sample movement.
limator tube. As the pressure increases and the gaskets thin down, the gap between the anvils becomes smaller than the beam width. This also tends to increase the exposure time, but, what is more serious, there is the danger of occasional lines from the carbide anvils being recorded on the diffraction pattern. This could be avoided by milling a groove on the anvil faces flanking the undeviated emergent beam, but would increase the ever-present danger of cracking an anvil at the higher pressures. It is preferable to employ an oversized cell of initial edge-length 1.91 cm with anvils of edge 0.635 cm, even though its use means a loss in pressure and an increase in exposure time due to absorption of the beam in the wider gasket. However, on account of the increased gasket thickness, the arrangement does have the advantage of yielding diffraction patterns which are about 0.25 cm wide at 100 kbar.

2.4. Exposure conditions

Because of the high absorption of the X-ray beam and the small volume of sample irradiated, the exposure periods with a monoxide + NaCl mixture range from about 4 to 10 hours, depending on the pressure, using unfiltered Ag K(α+β) radiation with the tube operating at 70 mA and 68 kV, a focal spot of area 0.05 x 1.0 cm, and with a beryllium screen of thickness 0.018 cm in front of the film (Ilford Industrial G). It was found that the exposure time could be reduced by a factor of 2½-3 with no appreciable loss in quality if Cronex 4 X-ray film (by DuPont) was employed, backed by a Type D Cronex X-tra Life miniature radiographic intensifying screen (blue fluorescence) (Herglotz, 1968).

Errors produced by sample movement and press-stretching

To avoid errors in lattice parameter determination due to film shrinkage, the Bradley & Jay (1932) arrangement was employed in which the film cassette is fitted with symmetrical knife edges which subtend a standard Bragg angle θ_k in the high-order region. The angle θ of any pair of lines on the film is related to S, the distance between the lines by the relation θ/θ_k = S/S_k, where S_k is the distance apart of the fiducial marks on the film produced by the knife edge shadows. For a cubic crystal such as TiO or NaCl, for example, the lattice parameter a is related to the wavelength within the crystal of the radiation λ, the Bragg angle θ, and the indices of reflection hkl by the equation

\[ a = \frac{\lambda}{2 \sin \theta} \sqrt{h^2 + k^2 + l^2} \]  

(1)

and the fractional error in a caused by errors in measuring θ, obtained by differentiating equation (1) is

\[ \frac{da}{a} = -\cot \theta \cdot d\theta \]  

(2)

If R is the radius of the camera, and S the distance between corresponding reflections on each side of the incident ray [Fig. 2(b)].

\[ S = 4R0, \] so that \[ dS = 4Rd\theta. \]

Hence

\[ \frac{da}{a} = -\frac{\cot \theta}{4R} \cdot dS. \]  

(3)

After aligning the beam accurately through the system by employing a series of brass tetrahedra with beam-localizing holes of decreasing size, and setting the film cassette at the exact radial distance \( R = 12.50 \) cm when the press is under its initial oil pressure of 4-2 kg/cm\(^2\) to remove all slackness from the joints, the major factors which contribute to the error \( dS \) are as follows:

(a) Eccentricity of the sample. This is partly due to the difficulty of locating the exact geometrical center of the cell. In addition, extrusion of the cell to form the gasket causes the sample to move off center.

(b) Apparent eccentricity due to X-ray absorption in a sample of finite thickness which results in a skew line-profile.

(c) Tie-bar stretching with increasing load. This causes the film cassette to move away from the center of the press and in the direction of the beam, thereby introducing an additional eccentricity error.
3.1. Errors produced by sample eccentricity and absorption

We shall first of all assume the sample to be located at the point $O$ [Fig. 2(b)] which initially represents both the center of the press and the center of the tetrahedral cell. As a result of the extrusion process, the sample will move away from the center of the press and in the direction of the beam through a distance $x$, which may be positive or negative, to the new position $O'$, and the symmetrical pair of rays deviated through the angles $2\theta$ will now strike the film in the points $bb$ instead of the points $aa$. The measured distance $S$ between the reflections will thus be too small by the amount $AS = 2ab = 2x \sin 2\theta$. From equation (3), the corresponding fractional error in $a$ will be,

$$\frac{da}{a} = -\frac{\cot \theta}{4R} \cdot (-2x \sin 2\theta) = \left(\frac{X}{R}\right) \cos^2 \theta.$$  

(4)

Thus the apparent lattice parameter will appear too large by the fractional amount $(x/R) \cos^2 \theta$ if the specimen moves toward the film and too small if it moves away.

The effect of absorption is to modify the line profile. This is a quantity which can neither be calculated nor measured easily. However, its effect is similar to having an additional increment in the value of $x$ and it may therefore be combined with the eccentricity error.

3.2. Error produced by tie-bar stretching

This error depends on the way in which the X-ray tube and film cassette are mounted. In the present set-up, as stated above, the tube is mounted on a cross-slide which is rigidly attached to the pedestal in which a ram base of the inverted press is lodged, while the film cassette is supported at the center of a tie bar as shown in Fig. 1. With this particular geometry, if the length of the tie bars is $L$, an increase $\Delta L$ produced by the load will cause the film and cassette to move away from the center of the press by the amount $\Delta L/2\sqrt{2}$. This is equivalent to a movement of the sample in the direction away from the film by the amount

$$x = -\frac{\Delta L}{2\sqrt{2}}$$  

(5)

and the corresponding apparent decrease in the lattice parameter will accordingly be

$$\frac{da}{a} = -\frac{\Delta L}{2\sqrt{2}} \cos^2 \theta.$$  

(6)

The value of $\Delta L$ can easily be measured as a function of oil pressure by attaching suitable strain gauges to the tie bars. In general, the correction for tie bar stretch is much smaller than that for sample eccentricity and is of the order of $0.01\%$ at most, whereas that due to eccentricity may be as high as $0.1\%$.

3.3. Extrapolation method for eliminating sample-movement errors

The total apparent fractional change in lattice parameter, $(da/a)_{total}$ will be the sum of three parts:

1. $(da/a)_p$ produced by the reduction in lattice parameter as a direct result of the applied pressure. Its value is a function of the compressibility of the material.
2. $(da/a)_e$ produced by sample movement due to extrusion. Its value is independent of the compressibility of the material.
3. $(da/a)_s$ produced by the elastic strain in the tie bars. Its value is also independent of the compressibility of the material.

Because we can determine $(da/a)_s = -\Delta L/2\sqrt{2} \cos^2 \theta$ by direct measurement, our problem reduces to determining $(da/a)_e$ in order to derive $(da/a)_p$ from the observed $(da/a)_{total}$.

On the up stroke, because of the initial oil pressure in the system, some extrusion of the cell causes an initial movement of the sample which cannot be computed from the NaCl spacing because we cannot compute the precise pressure within the cell. As the pressure increases and more gasket forms, the displacement $x$ will increase. This movement is not a linear function of the load and so values of $(da/a)_e = (x/R) \cos^2 \theta$ will be indeterminate on the up-stroke. If, on the other hand, the applied pressure is taken to its maximum, the displacement $x$ will also attain its maximum. Because the additional amount of extrusion will be negligible on the down stroke, it may be safely assumed that $x$, and
hence \((da/a)_e\) will be constant for all down stroke pressures. Our problem, then, is to determine \((da/a)_e\) at zero pressure when, because of the construction of the press, we must provide a minimum oil pressure of about 4-2 kg.cm\(^{-2}\) on the rams (corresponding to about 9 kbar on a sample in a cell of initial edge 0.635 cm) in order to keep the anvils closed and the tie bar joints tight.

If the zero pressure could be reached, the calibration medium NaCl and the admixed monoxide would each display the same fractional parameter change, which would be equal to

\[
\left( \frac{da}{a} \right)_e = \left( \frac{x}{R} \right) \cos^2 \theta.
\]

We can therefore plot a graph of \((da/a)\) for NaCl versus corresponding values of \((da/a)\) for the monoxide, and where the curve intersects the line \((da/a)_{NaCl} = (da/a)_{oxide}\) we obtain the value of \((da/a)_e\) for zero load. We can then use this value along with the computed values of \((da/a)_e\) to determine \((da/a)_p\) from the observed value of \((da/a)_{total}\) for any load on the down stroke. A typical plot is shown in Fig. 3 for vanadium monoxide, for a cell of edge length 0.635 cm. It is interesting to note that the movement of the sample can be in such a direction that, at low pressures and in the absence of the eccentricity correction, the NaCl standard will seem to be under pressure while the monoxide will seem to be under tension. This anomaly appears for experimental points which fall in the second quadrant of Fig. 3. On the other hand, if the eccentricity is such that the intersection occurs in the first quadrant, both the standard and the sample will appear to be compressed at all pressures.

### 4.1. Compressibility of titanium monoxide

Fig. 4 illustrates the compressions of (TiO)\(_{0.856}\) (\(\square\)\(_{0.144}\)) and (TiO)\(_{1.000}\) (\(\square\)\(_{0.000}\)) and of the standardizing material NaCl, which is based on the work of Decker (1965, 1968). The lattice compressions \(\Delta a/a\) for the vacancy-containing and vacancy-free forms are small compared with that of NaCl and differ very little from each other, the values of the compressibilities \(\kappa = 1/p\ \Delta e/\Delta v = 3/p \ \Delta a/a\) being 5-4 (3) \(\times 10^{-13}\) cm\(^2\).dyne\(^{-1}\) for (TiO)\(_{0.856}\) (\(\square\)\(_{0.144}\)) and 5-1 (0) \(\times 10^{-13}\) cm\(^2\).dyne\(^{-1}\) for (TiO)\(_{1.000}\) (\(\square\)\(_{0.000}\)). These compressibilities are beginning to approach the value for diamond, namely 1-8 \(\times 10^{-13}\) cm\(^2\).dyne\(^{-1}\) obtained isothermally by Drickamer (1966) and 2-26 \(\times 10^{-13}\) cm\(^2\).dyne\(^{-1}\) obtained ultrasonically by McSkimin & Bond (1957).

Subsequent to our work on the compressibility of TiO, VO and NbO, which has been briefly reported (Taylor & Doyle, 1970), Iwasaki, Kamigaki, Ogawa, Terasaki & Watanabe (1970) have some compression results on TiO\(_{1.32}\) which lies at the oxygen-rich boundary of the TiO phase. These workers employed a tetrahedral anvil press combined with an X-ray diffraction equipment of a type not described, and used NH\(_4\)Cl as a marker. Their plot of \(a/a_0\) versus pressure up to 60 kbar shows an initial increase in \(a/a_0\) up to 10 kbar, after which it begins to decrease. This precisely the effect we should anticipate if no correction is made for tie bar stretch and for sample movement as illustrated in Fig. 3. Their value of \(K = 8.6 \times 10^{-13}\) cm\(^2\).dyne\(^{-1}\), obtained by disregarding data below 10 kbar is substantially greater than our value of 5-4 (3) \(\times 10^{-13}\) cm\(^2\).dyne\(^{-1}\) for (TiO)\(_{0.856}\) (\(\square\)\(_{0.144}\)). This difference may be due in part to the errors introduced by failure to correct for sample movement and, in part, to compositional differences. These points further exploration. Another factor which may need exploration is the relative merits of NaCl and NH\(_4\)Cl markers for materials with such low compressibilities as TiO.

### 4.2. Compressibilities of vanadium and niobium monoxides

The lattice compressions for (VO)\(_{0.848}\) (\(\square\)\(_{0.152}\)) and (NbO)\(_{0.750}\) (\(\square\)\(_{0.250}\)) are presented in Fig. 5 along with the compression curve of (TiO)\(_{0.856}\) (\(\square\)\(_{0.144}\)). As may be seen from the Figure, the compression curves are linear within the range of experimental accuracy. The compressibility coefficient \(\kappa\) for the vanadium oxide is 6-3 (8) \(\times 10^{-13}\) cm\(^2\).dyne\(^{-1}\), which is about 17% higher than for (TiO)\(_{0.856}\) (\(\square\)\(_{0.144}\)). On the other hand the value of \(\kappa\) for niobium monoxide is 4-2 (6) \(\times 10^{-13}\) cm\(^2\).dyne\(^{-1}\) which is almost 22% lower. This would indicate that the bonding in the niobium monoxide is much stronger than in the other two despite its much larger number of lattice vacancies. Combined with the fact that the combined action of pressure and temperature (within the range of the present experiments) seems to have no influence whatever on the vacancy concentration in NbO or on the ordered arrangement, it would seem that the

![Fig. 5. Relative compressions of (TiO)\(_{0.856}\) (\(\square\)\(_{0.144}\)), (VO)\(_{0.848}\) (\(\square\)\(_{0.152}\)) and (NbO)\(_{0.750}\) (\(\square\)\(_{0.250}\)).](image-url)
A. TAYLOR AND N. J. DOYLE

Table 1. Grüneisen constants

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(TiO)(<em>{0.856})((\square))(</em>{0.144})</td>
<td>20.3 x 10(^{-6})</td>
</tr>
<tr>
<td>(VO)(<em>{0.848})((\square))(</em>{0.152})</td>
<td>28.08 x 10(^{-6})</td>
</tr>
<tr>
<td>(NbO)(<em>{0.750})((\square))(</em>{0.250})</td>
<td>14.61 x 10(^{-6})</td>
</tr>
</tbody>
</table>

(a) Computed from \(C_P - C_v = \left(9a^2V/k\right)T\) (b) Shomate (1946) (c) Todd & Bonnickson (1951) (d) Kelley & King (1961) (e) Gel’d & Kusenko (1960) (f) Toriloukian (1967)

vacancies are an inherent part of the structure and are not lattice defects as normally envisaged.

4.3. Grüneisen constants

Using our own data on the thermal expansions, compressibilities and molecular volumes, and published specific heat data, we have computed the Grüneisen constants \(\gamma\) for (TiO)\(_{0.856}\)(\(\square\))\(_{0.144}\), (VO)\(_{0.848}\)(\(\square\))\(_{0.152}\) and (NbO)\(_{0.750}\)(\(\square\))\(_{0.250}\). The published specific heats \(C_P\) are for constant pressure. These were converted to the specific heats at constant volume \(C_v\) by means of the well-known expression

\[
C_P - C_v = \left(9a^2V/k\right)T
\]

where \(a\) is the coefficient of linear expansion, \(V\) the molecular volume, \(k\) the compressibility and \(T\) the absolute temperature. The correction is small, being of the order of 2\%, at most.

The computed values of the Grüneisen constants are presented in Table 1 along with the corresponding thermal and mechanical constants. As may be seen from the Table, the value of \(\gamma\) for (TiO)\(_{0.856}\)(\(\square\))\(_{0.144}\) and (VO)\(_{0.848}\)(\(\square\))\(_{0.152}\) are virtually identical, namely 1.20 (5) and 1.21 (5) respectively, whereas the value for (NbO)\(_{0.750}\)(\(\square\))\(_{0.250}\) is 5\% higher at 1.26 (0).

References


