THE COMPRESSIBILITY OF SODIUM TUNGSTEN BRONZES

Jiří VONDRÁK[a] and Jozef ZÁMEČNÍK[b]

[a] *Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 160 00 Prague 6 and*
[b] *Faculty of Construction, Slovak Institute of Technology, 884 20 Bratislava*

Received September 18th, 1979

The linear compressibility of cubic sodium tungsten bronze Na_xWO_3 ($x = 0{\cdot}72$) is $(-8{\cdot}56 \pm \pm 0{\cdot}54) \cdot 10^{12}$ Pa^{-1}; the linear compressibility of type I tetragonal bronze ($x = 0{\cdot}46$) is $(-20{\cdot}2 \pm \pm 1{\cdot}3) \cdot 10^{12}$ Pa^{-1} parallel to the *a*-axis and $(+4{\cdot}17 \pm 1.9) \cdot 10^{12}$ Pa^{-1} parallel to the *c*-axis. The compressibility of cubic bronze decreases somewhat with increasing pressure (in the range 0—250 mPa). The compressibility was directly measured optically.

Depending on the sodium content and the preparation conditions, sodium tungsten bronzes, Na_xWO_3, form a number of modifications. At sodium contents from 0 to $x = 0{\cdot}12$ monoclinic, rhombic and type II tetragonal modifications are formed. At higher sodium contents ($0{\cdot}28 < x < 0{\cdot}5$) tetragonal type I modification is formed and, at sodium contents of $0{\cdot}4 < x < 1$, the cubic form with perovskite lattice is present[1]. The lattice constant and thus the molar volume of these substances depends linearly on the sodium content[1-3]. This lattice expansion can be related through the volume compressibility $\varkappa_V = -1/V \cdot (\partial V/\partial p)_T$ to the internal energy of the system U by the familiar expression

$$K = 1/\varkappa_V = V \cdot (\partial^2 U/\partial V^2) \cdot T \qquad (1)$$

and thus the activity coefficient of sodium in Na_xWO_3 bronze can be derived[7]. The numerical value of the compressibility is necessary for this calculation. This work is concerned with the determination of this value.

EXPERIMENTAL

Na_xWO_3 single crystals were prepared electrolytically by cathodic reduction of a fused mixture of Na_2WO_4 and WO_3 at temperatures about 20°C above the solidification point; in this way, crystals with dimensions of 10—20 mm can readily be prepared. Details on the preparation and chemical analysis of bronzes are given elsewhere[4].

Measurement of the Linear and Volume Compressibility

The effect of overall pressure results in a change of arbitrary dimension h_0 by Δh. The coefficient of linear compressibility $\varkappa_h = -1/h_0 \, . \, \partial h/\partial P$ in isotropic substances is independent of the direction and roughly also of the pressure or relative compression. Thus it is necessary to measure the linear compressibility in all significant directions in crystalline substances. Thus, in cubic bronze we measured the longitudinal compressibility $\varkappa_a$ along the *a*-axis and in tetragonal bronze along the *a*- and *c*-axes ($\varkappa_a$ and $\varkappa_c$). The volume compressibility was found from the relationship $\varkappa_V = 3\varkappa_a$ or $\varkappa_V = 2\varkappa_a + \varkappa_c$.

The longitudinal compressibility was measured by the direct optical method[5,6]. The dependence of the relative change in length $\Delta h/h$ on pressure p is depicted in Fig. 1. All the three dependences are approximately linear and can thus be described by the equation

$$P = K_i \, . \, \Delta h/h = 1/\varkappa_i \, . \, \Delta h/h \, , \qquad (2)$$

where $\varkappa_i$ and K_i are the longitudinal compressibility and the module of longitudinal compres-

TABLE I

Longitudinal Compressibility $\varkappa$ and Longitudinal Modules K' and K'' for Sodium Tungsten Bronzes Na_xWO_3

x	Structure	orientation	$\varkappa \, . \, 10^{-12}$, Pa^{-1}	$K' \, . \, 10^{10}$, Pa	$K'' \, . \, 10^{12}$, Pa
0·72	cubic	‖ a	−8·56 ± 0·54	−4·6 ± 2·5	44·17 ± 16·7
0·46	tetrag. I.	‖ a	−20·2 ± 1·3	−2·9 ± 1·2	4·8 ± 3·2
0·46	tetrag. I.	‖ c	+ 4·17 ± 1·9	+4·3 ± 4·5	26·6 ± 29·4

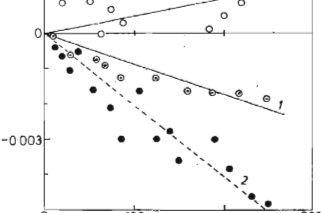

FIG. 1

Dependence of the Relative Linear Change $\Delta h/h$ on Pressure p

1 Cubic bronze $Na_{0.72}WO_3$, *2* tetragonal bronze I with composition $Na_{0.46}WO_3$ along the *a* axis, *3* the same bronze along the *c* axis.

sibility along the *i*-axis. Because the measured dependence of the pressure on the relative compression $\Delta h/h$ was not completely linear, the quadratic dependence

$$P = K_i' \cdot (\Delta h/h) + K_i'' \cdot (\Delta h/h)^2 , \qquad (3)$$

was also used for correlation of the measured relationships. Table I gives the calculated values of $\varkappa_i$, K_i' and K_i'' along with the reliability estimate for all the measured samples. The precision of the estimate of the coefficient of the quadratic term K_i'' is not statistically significant, as can be seen from the table; thus the volume compressibilities were calculated using the linear compressibilities defined by linear relationship (*2*); coefficients K' and K'' were not considered further. Compressibilities $\varkappa_V = (2{\cdot}57 \pm 0{\cdot}16) \cdot 10^{-11}$ Pa^{-1} for cubic bronze and $\varkappa_V = (1{\cdot}017 \pm 0{\cdot}3) \cdot 10^{-11}$ Pa^{-1} for tetragonal bronze were found in this way.

DISCUSSION

Cubic Bronze

The measured value of the volume compressibility is of the same order as the predicted value $\varkappa_V = 1{\cdot}5 \cdot 10^{-11}$ Pa^{-1}, which follows from the thermodynamic analysis of tungsten bronzes[7].

The Grüneisen constant

$$\gamma = 3V \cdot \alpha/(\varkappa_V \cdot C_p) = 0{\cdot}377 \qquad (4)$$

can be obtained from the values of the lattice constant $a = 0{\cdot}3843$ (*i.e.* molar volume $V_M = 3{\cdot}4197 \cdot 10^5$ m^3/mol), of the specific molar heat found from interpolation of the Inabe data[8], $C_p = 92{\cdot}4$ kJ kg mol K^{-1} and from the coefficient of longitudinal expansion given by Smith and Danielson[9], $\alpha = 8{\cdot}31 \cdot 10^{-6}$ K^{-1}. Substitution of a value of $\alpha = 11{\cdot}6 \cdot 10^6$ (Takamori and Tomozawa[10]) for the expansion coefficient yields a value of $\gamma = 0{\cdot}496$.

This value is somewhat lower than the usual value of 1–2, found for simpler compounds with lower specific heats and lower Debye temperatures than that of tungsten bronze[11]. The Born–Landé equation yields the quantity

$$|U_0|\, mn = 9/\varkappa_V \cdot V_0 = 11{\cdot}7 \cdot 10^6 \text{ kJ/kmol} , \qquad (5)$$

where m and n are the exponents for the dependence of the attractive and repulsive forces between ions in the Mie relationship for energy U_0 for two ions at a distance of r:

$$U_0 = A/r^m - B/r^n . \qquad (6)$$

Coefficient m is generally considered to be equal to 1 as the attractive forces have the character of Coulomb forces.

Tetragonal Bronze

Tetragonal bronze is remarkable in that the effect of overall pressure results in elongation along the *c*-axis. This effect is a result of the marked anisotropy of this material; the sum of elongation along the *c*-axis as a result of pressure along both *a*-axes is apparently greater than the compression in the same direction produced by pressure along the *c*-axis. These bronzes have a tunnel structure in which the basic octahedral WO_6 structural units are deformed. The overall structure of these substances is exposed to internal strain, which leads to the described peculiarity and anisotropy and results in the marked energy consumption (20–40 MJ/kg mol) necessary for the formation of hypothetical WO_3 with type I tetragonal structure (without sodium) from the low temperature monoclinic formation WO_3.[4] The fact that the volume compressibility of these bronzes is less than that of cubic bronzes is in agreement with this finding. The value

$$|U_0| \,.\, mn = 2{\cdot}9 \,.\, 10^7 \text{ kJ/kg mol}$$

follows from the Born–Landé relationship for this type of bronze.

The Dependence of the Volume Compressibility on the Relative Compression

As can be seen in Fig. 1, the observed dependence of the longitudinal compression on the pressure is not completely linear. Thus an attempt was made to derive the dependence of the compressibility module on the pressure in a similar manner to that employed in derivation of the Born–Landé equation (5).

Let U be the internal energy of a system in volume V; it then holds for small volume changes that

$$U \approx U_0 + (\mathrm{d}U/\mathrm{d}V)_{V_0} \,.\, \Delta V + 1/2(\mathrm{d}^2U/\mathrm{d}V^2)_{V_0} \,.\, \Delta V^2 + 1/6(\mathrm{d}^3U/\mathrm{d}V^3)_{V_0} \,.\, \Delta V^3 \,. \quad (7)$$

The molecular volume of a substance with perovskite lattice and lattice constant r is then

$$V = N \,.\, r^3 \quad (8)$$

and, at equilibrium, the condition $\mathrm{d}U/\mathrm{d}V = 0$ is valid. If derivative $\mathrm{d}U/\mathrm{d}V$ in equation (7) is expressed using relationship (8), by introducing lattice constant r_0 and using the Mie equation (6), then the required dependence of the pressure on the relative volume $\Delta V/V$ is obtained:

$$p = -K' \,.\, \Delta V/V_0 - K'' \,.\, (\Delta V/V_0)^2 \,. \quad (9)$$

In this relationship coefficient K' represents the module of volume compressibility

at zero pressure, described by the modified Born–Landé equation (5):

$$K' = mn/9V_0 \,.\, |U_0| \qquad (10)$$

and the value

$$K'' = K' \,.\, (n + m - 3)/6 \qquad (11)$$

or

$$K''/K' = 1/6 \,.\, (n + m - 3) \qquad (12)$$

is obtained for coefficient K''.

Table I indicates that the value of coefficient K_p for cubic bronze is by an order larger than the value following from equations (11) and (12). Thus the compressibility of cubic bronze is not exactly described by the Hooke law. Thus the interatomic forces of repulsion in this substance increase under compression faster than determined by term $-B \,.\, r^{-n}$ in the Mie equation (6). The confidence limits of this coefficient are, however, rather broad ($\pm 40\%$) and the phenomenon of nonlinear compression can be much less then corresponds to the mean value of coefficient K'' in Table I.

This phenomenon is of much smaller magnitude for tetragonal bronze. The K'' coefficients in both directions are much smaller than for cubic bronze. Thus the confidence limits of coefficient K'' are comparable with its magnitude and thus the Hooke law is valid within the precision limits of the experiment for this type of bronze.

REFERENCES

1. Hagenmuller P. in the book: *Non-Stoichiometric Compounds: Tungsten Bronzes, Vanadium Bronzes and Related Compounds.* (D. J. M. Bevan, P. Hagenmuller, Eds), p. 541. Pergamon Press, New York 1973.
2. Brown B. W., Banks E.: J. Amer. Chem. Soc. *76*, 963 (1954).
3. Reuland R. J., Voight A. F.: Inorg. Chem. *35*, 1263 (1963).
4. Vondrák J., Balej J.: Electrochim. Acta *18*, 1017 (1973).
5. Zámečník J.: Unpublished results.
6. Zámečník J.: Česk. Čas. Fyz. *A29*, 482 (1979).
7. Vondrák J.: J. Chem. Soc., Faraday Trans., in press.
8. Hideaki Inabe, Keiji Naito: J. Solid State Chem. *15*, 283 (1975).
9. Smith J. F., Danielson G. C.: J. Chem. Phys. *22*, 266 (1959).
10. Takamori T., Tomozawa M.: J. Amer. Ceram. Soc. *47*, 272 (1974).
11. West R. W., Griffel M., Smith J. F.: J. Chem. Soc. *28*, 293 (1955).

Translated by M. Štulíková.