Appendix 6 of ref. 10 and in Tables 4 and 5 of ref. 11) were: 0.000160, 0.00146, 0.0119, 0.0733 and 0.332. When solutions of nominally identical activities were placed in each of the electrode compartments the residual emf fell in the range 0.5 to 2.5 mV. The reading was even less (< 0.1 mV) when the β-alumina crystals were mounted with their basal planes parallel to the crystal-solution interface, even with log $(a_\pm)_1/(a_\pm)_2$ ratios as large as 3.32.

Fig. 2 shows the observed dependence of emf upon the logarithm of the activity ratio at 298 K, with the β-alumina crystal in the conductivity orientation. The slope is $(0.0568 \pm 0.0025)\ V$ ($2.303\ RT/F = 0.05916 V$ at 298 K).

A similar set of measurements carried out using various strengths of aqueous NaCl solutions (mean activities in the range 0.000102 to 0.691) as the electrodes yielded a plot similar to that shown in Fig. 2, the slope being $(0.0598 \pm 0.0070)\ V$.

No attempt was made to explore the pH-dependence of these concentration cells, but present work clearly indicates that β-alumina could be utilized as a form of "sodium ion-sensitive electrolyte" when the pH is close to 7. A few experiments were, however, carried out on the H_3O^+ form of β-alumina (where the sodium is replaced by hydrogen ions – prepared as described by Yao and Kummer [12]), aqueous sulphuric acid solutions (molalities from 0.0000103 to 0.0974) being used as electrodes. Again anisotropic-concentration cell behaviour was observed, though the results were rather less reproducible.

It is not irrelevant to comment that mechanically robust single crystals of highly-anisotropic solid electrolytes, used in the configurations described above, could function as useful electrical switching devices in certain technological applications.

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Apparatus to measure single crystal elastic constants over a wide range of temperature (RT - 1400 K)

It is desirable for many applications to know the elastic constants of materials over a wide range of temperature. This paper describes an apparatus for high temperature measurements which is relatively easy to construct. The method used to measure the elastic constants is the thin rod resonance technique [1]. In this the specimen is excited and the resonant frequencies used to calculate the elastic constants. The arrangement is shown diagrammatically in Fig. 1. A and B are the exciting and detecting transducers. A fine untensioned wire is used to transmit vibrations to and from the specimen. All modes of vibration – longitudinal, transverse and torsional may be simultaneously excited. Depending upon the particular coupling geometry, one mode may be favoured more than the others.

The "acoustic assembly" used for measurements at room-temperature is similar to that used by other workers. It consists essentially of

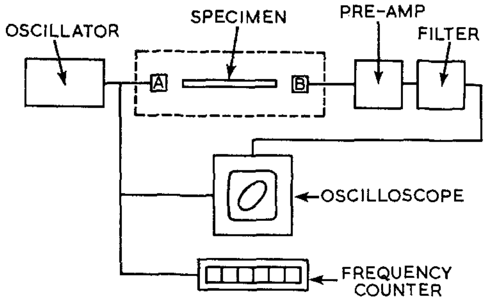

Figure 1 Block diagram for measurement of elastic constants by resonance technique.

three adjustable supports, one for each of the transducers and one for the specimen. The transducers are magnetically clamped to the supports. The angles of the coupling wires are easily changed to favour one particular mode of vibration. The receiving piezoelectric crystal does not measure resonance directly but relative movement between its anchorage and that part of the specimen to which it is coupled via the fine wire. The assembly is designed to minimize relative movement caused by any means other than the vibration of the specimen. Spurious vibrations can give rise to "apparatus" resonances. The sources of such vibrations must be eliminated as far as possible or the vibrations dampened out. This is possible to a large extent in the room-temperature apparatus but very difficult at high temperatures.

In the high-temperature apparatus (Fig. 2) the acoustic assembly must be enclosed in an evacuated chamber to prevent oxidation. Consequently it must be much more compact. The problems associated with specimen damping and spurious resonances thus become more acute. To overcome specimen damping thicker coupling wires are used; if the coupling wires are too thick they must be considered part of the resonating system and the natural resonant frequencies are displaced from their true values. Filters are necessary to remove unwanted frequency ranges from the display. Nevertheless, faint specimen resonance and spurious vibrations can make measurement and identification of resonances very difficult in certain temperature ranges.

The acoustic bench was designed to fit into an industrial Pyrex Glass "X" – section. One limb rests on a conventional pumping system. The two end plates house the vacuum lead-throughs for the electrical connections, the vacuum-gauge and the facility for fine adjustment of the coupling wires. The furnace element is screened by a stainless steel tube and a water cooled

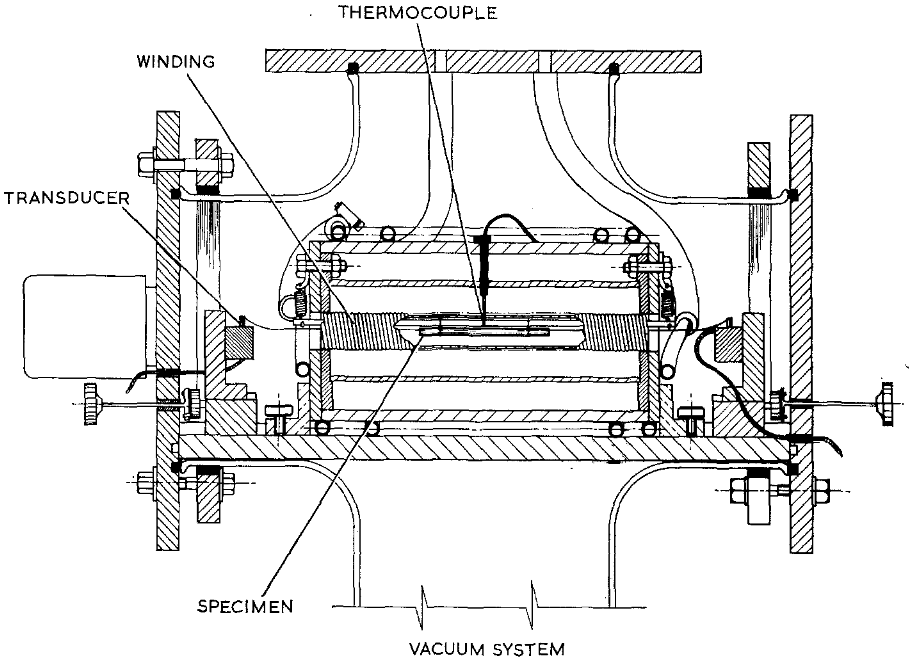

Figure 2 Section drawing of high-temperature apparatus.

copper tube. The water connections are made via the top plate.

The coupling wires, usually tungsten, are spot-welded onto the specimen. The angle formed ensures that torsional resonances are induced as well as the longitudinal. The specimen is not clamped but is instead slung beneath a molybdenum rod by means of two spot-welded loops of fine wire. Both the rods are passed through the narrow bore (10 mm diameter) furnace tube (an electric fire-element former with a tungsten winding). The supporting rod is chosen to be longer than the element and the projecting ends are secured by small springs. If the suspension loops have been made to the correct size then the slight bending which occurs ensures that the specimen is suspended freely and coaxially within the element. The length of the element (200 mm) is chosen to be at least twice that of the longest specimen (100 mm). This ensures a uniform specimen temperature. During tests no temperature difference was detected along the length of a dummy specimen. The temperature of the actual specimen during an experiment is obtained from a thermocouple secured at the centre of the support rod.

The relationships between the resonant frequencies and the elastic constants are [2]: longitudinal

$$E = \frac{4l^2 f_l^{\,2} \rho}{n^2} (1 + \alpha \Delta T)^{-1} / K_n \qquad (1)$$

torsional

$$G = \frac{4l^2 f_t^{\,2} \rho}{n^2} (1 + \alpha \Delta T)^{-1} \qquad (2)$$

where $K_n = 1 - (\pi^2 n^2 p^2 d^2 / 8l^2)$, l is the length of the specimen, f_l, f_t the resonant frequencies in longitudinal and torsional modes respectively, ρ the density, α the average coefficient of thermal expansion, ΔT the temperature difference, n the harmonic, p Poisson's ratio, and d the diameter. The second term for the longitudinal and torsional resonances takes into account the change in length and density using an average coefficient of thermal expansion. A correction, K_n is also made for the lateral contraction of the rod when undergoing longitudinal vibrations.

The resonant frequencies of a single crystal depend upon the orientation of the specimen axis. The Young's modulus or shear modulus obtained from Equations 1 and 2 is related to the elastic compliance constants as in Equations 3 and 4. There are only three independent constants S_{11}, S_{12} and S_{44} for crystals with cubic symmetry

$$1/E_H = S_{11} - (2(S_{11} - S_{12}) - S_{44}) H \qquad (3)$$

$$1/G_H = S_{44} + 2(2(S_{11} - S_{12}) - S_{44}) H \qquad (4)$$

where

$$H = \cos^2 \alpha \cos^2 \gamma + \cos^2 \beta \cos^2 \gamma + \cos^2 \alpha \cos^2 \beta$$

and α, β and γ are the angles between the specimen axis and the cube axes. Thus, to solve the simultaneous equations, at least two specimens of different orientation are required and resonant frequencies for both torsional and longitudinal vibrations must be determined. An analysis of the sources of error shows that $\langle 001 \rangle$, $\langle 011 \rangle$ and $\langle 111 \rangle$ crystals allow the most accurate results to be computed from the measured data.

The elastic constants are first determined in the room-temperature apparatus. The approximate resonant frequencies are computed using the Equations 1 to 4 if the elastic constants can be estimated. This is a great help in differentiating between real and spurious resonances. Nevertheless, identification can sometimes prove difficult, when an estimate of the damping must be made. Specimen resonances usually decay more slowly than spurious resonances. In addition, the measurements are repeated after the specimen has been shortened. True specimen resonances should then occur at different frequencies, which can be predicted.

Examination of Equations 3 and 4 shows that

$$\left(\frac{1}{E_H} + \frac{1}{2G_H} \right)$$

is a constant independent of orientation. At a given temperature, if the correct measurement and identification of resonances have been made, then each rod of the same composition should produce the same constant or "consistency factor".

Measurements are then conducted in the high-temperature assembly. The room-temperature measurements are used to predict the temperature-dependence of the resonant frequencies to assist identification at high temperatures. Two separate excitation networks with a change-over switch are used so that two different resonances (e.g. longitudinal fundamental and torsional fundamental) can be followed simultaneously as the temperature is varied This is much simpler than measuring at discrete temperatures with no intermediate observation. The frequency of resonance is recorded at regular temperature intervals.

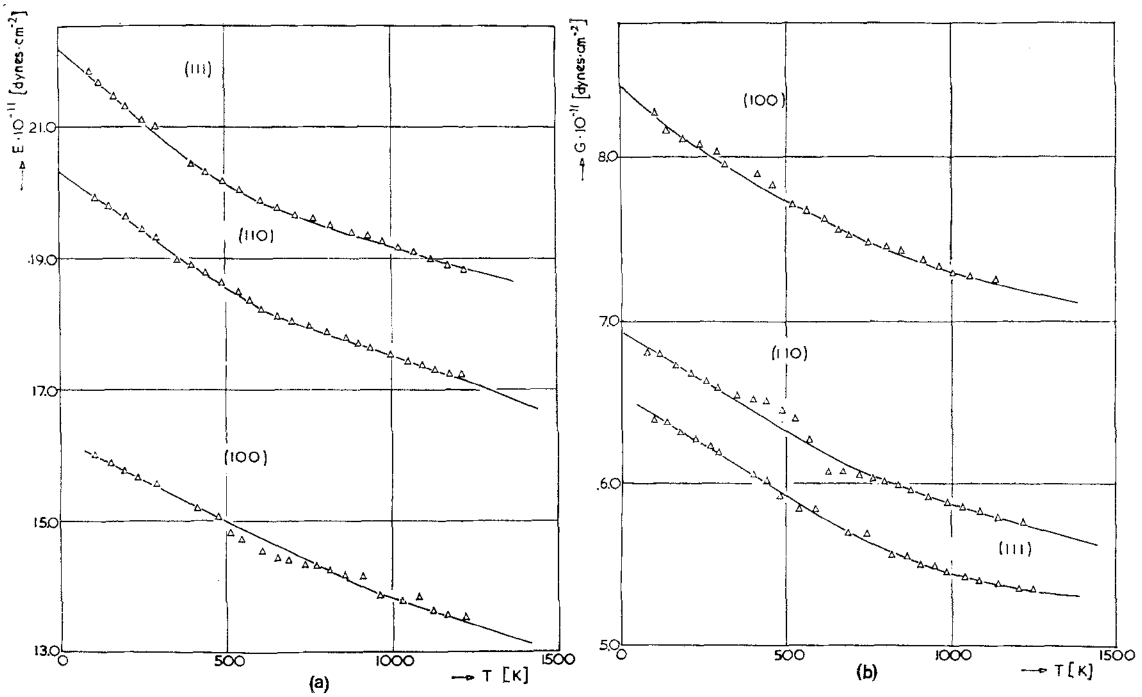

Figure 3 Effective moduli against temperature for Ta 4% Mo single crystals.

The consistency factor for each orientation should exhibit the same temperature-dependence. A full discussion of the evaluation as applied to tantalum crystals is given elsewhere [3]. Fig. 3 shows typical results attainable with this apparatus. The moduli as calculated from Equations 1 and 2 are plotted for each orientation as a function of temperature. Also included in Fig. 3 are low-temperature and room-temperature results from other apparatus. The good agreement of the room-temperature measurements obtained using different apparatus indicates that the loading in the high-temperature apparatus is negligible. It can be seen that in the temperature range 500 to 600 K points did not lie on the smooth curve. This was particularly true for the torsional vibrations which are more difficult to excite. In this range the specimen damping is excessive, probably due to interstitial impurities, and this makes measurement very difficult. It is, however, purely a specimen effect and is not observed with other types of material, for example with iridium.

The accuracy obtained with this apparatus relies on first establishing good room-temperature values and then using the high temperature apparatus to establish the temperature-dependence of various constants, e.g. S_{11} and S_{44} from $\langle 001\rangle$ crystals or S_{12} from $\langle 110\rangle$ crystals. Used in this way, the results are much more reliable than those obtained by solving the simultaneous equations at different temperatures using the information contained in Fig. 3. Extensive use of computers is necessary to predict the frequency ranges where resonance is expected, to evaluate the results, and to carry out an error analysis.

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