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Elastic Moduli of ReO_3 by Brillouin Scattering

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Brillouin light scattering has been used to measure elastic stiffness constants in the metal ReO_3: $c_{11} = (71.7 \pm 3.5) \times 10^{11}$ dynes/cm^2, $c_{44} = (7.11 \pm 0.25) \times 10^{11}$ dynes/cm^2, and $c_{12} = (10.3 \pm 3.4) \times 10^{11}$ dynes/cm^2. These values are significantly higher than those obtained ultrasonically at room temperature by Pearsall and Coldren. Since the Brillouin study employs light which heats the scattering volume, it probes lattice forces at an effectively higher temperature. Additional data taken at lower light intensity confirms the positive acoustic velocity temperature gradient.

Introduction

Rhenium trioxide is a transition metal oxide having lattice properties which can be thought of as fundamental to an understanding of the elastic behavior of the broad class of tungsten bronze materials. The ReO_3 structure, P_{m3m}, is simple cubic with the rhenium atoms situated at the cube vertices. As shown in Fig. 1, six oxygen atoms ocupy octahedral symmetry sites about each rhenium atom and are located at the midpoints of the cubic edges. This arrangement is characterized by a low packing density with highly directional bonds and leaves a large unoccupied space in the center of the cell. In the sodium tungsten

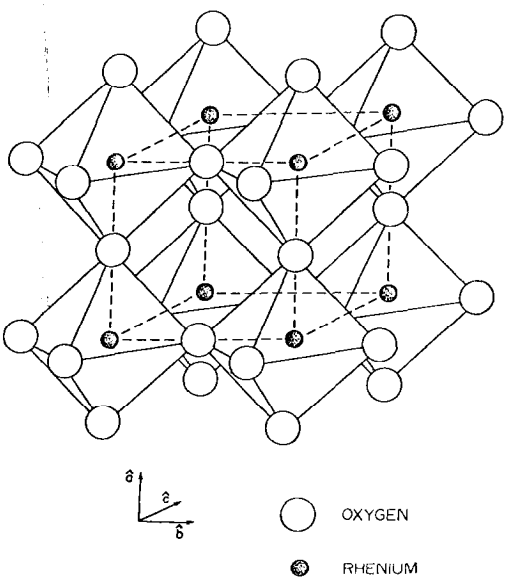

FIG. 1. Schematic representation of the ReO_3 structure showing cubic arrangement of ReO_6 octahedra. The structure has a large unoccupied space in the center of the cell.

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bronze group, Na_xWO_3 having $0.5 < x < 1$, the sodium atoms occupy this space forming the ideal perovskite structure in the limit $x = 1$.

The occurrence of important lattice associated properties such as superconductivity and ferroelectricity in the alkali metal tungsten bronzes, A_xWO_3, warrants a close examination of the elastic properties of these materials and the basic ReO_3 lattice. Elastic moduli give insight into the nature and strength of interatomic crystalline bonding and provide a means of correlating measured cohesive forces with observed physical properties. A systematic study of elasticity in the alkali bronzes has been hindered by several factors including the inability to grow sufficiently homogeneous single crystals of some of the most interesting compositions. ReO_3 is a good material with which to initiate a detailed study because it is stoichiometric, cubic, and structurally analogous to the tungsten bronze host lattice, WO_3. Elastic constants have recently been reported for ReO_3 by Pearsall and Coldren (*1*) and by Tsuda *et al.* (*2*).

Experimental Measurements

In the present investigation, single crystal samples were prepared by iodine vapor transport. The electrical resistivity at 300°K was 9.5×10^{-6} Ω-cm with a resistivity decrease by a factor of 500 at 4.2°K. Mass spectrographic analysis showed no elemental impurity in excess of 50 ppm (*3*). Samples were cubic, with dimensions of 1 mm on each side.

The Brillouin scattering technique can be used to investigate longitudinal and transverse acoustic phonons having a frequency in the range 150 to 500 GHz, which is between the measurement capabilities of ultrasonics and neutron scattering. It is nondestructive, requires no physical contact with the sample, and utilizes visible radiation. Studies of single crystal samples with dimensions of 100 μm are possible. The sound velocity, v, can be determined from two relationships. The first is that the propagation vector of the sound, $\mathbf{q}$, is determined by the Bragg condition for the incident and scattered propagation constants $\mathbf{k}_i$ and $\mathbf{k}_s$ of the light in the material,

$$\mathbf{q} = \pm(\mathbf{k}_i - \mathbf{k}_s). \tag{1}$$

The scattered light contains both a Doppler upshifted and a Doppler downshifted frequency. The magnitude of the angular frequency difference between the scattered and incident light, $2\pi\Delta\nu$, is the angular frequency of the sound, ω. Using the dispersion relation for sound propagation we obtain

$$v = \omega/q. \tag{2}$$

Traditionally, Brillouin scattering studies have been limited to transparent materials. However, with recent improvements in technique, it has become possible to obtain spectra from opaque, metallic ReO_3. In absorbing materials, the expressions for $\mathbf{k}_i$ and $\mathbf{k}_s$ are complicated and require knowledge of the complex refractive index, $\tilde{n} = n - i\kappa$, and the angles of incidence and observation (*4*). The exact expressions have been used in our computations. In the case of ReO_3 the excitation energy of our light source exceeds the plasma frequency and $n \gg \kappa$ (*5*). In such a situation, it is an excellent approximation to neglect κ, and then Eqs. (1) and (2) combine to give

$$v = \Delta\nu\lambda_0/[2n \sin(\phi/2)], \tag{3}$$

λ_0 is the wavelength of the incident light and ϕ is the angle between $\mathbf{k}_i$ and $\mathbf{k}_s$.

Measurements were made using the 488-nm wavelength of an argon laser. The optical constants of the crystal studied were determined by modulation ellipsometry (*5*). The complex refractive index at 488 nm was $\tilde{n} = 1.68 - i0.37$. Since the crystal was too absorbing to allow transmission, or forward scattering, all of our data were obtained in back scattering (*6*). The incident laser power was kept at or below 100 mW to avoid surface degradation. At 488 nm the calculated amplitude penetration depth of the incident light was 210 nm.

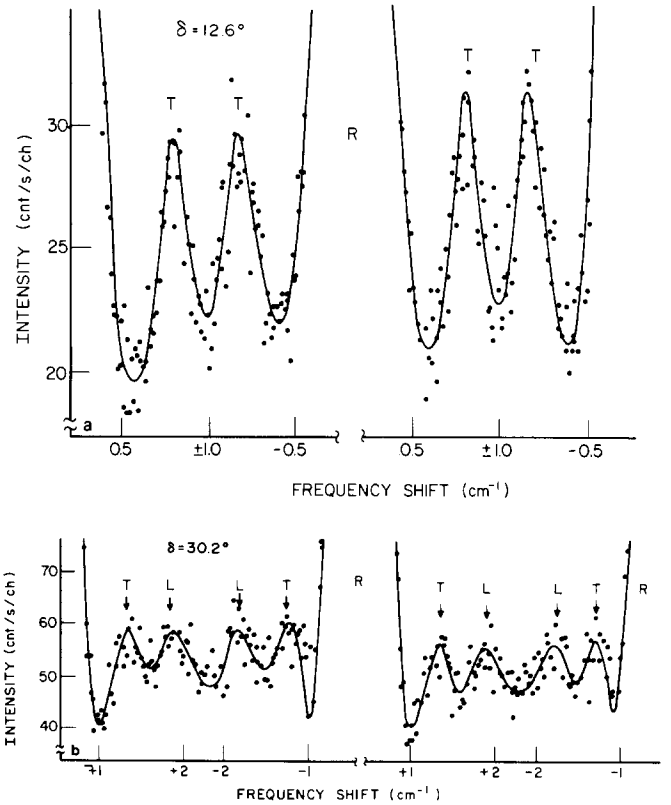

FIG. 2. Brillouin spectra from ReO_3 at 300°K for two phonon propagation directions, **q**, each making angle δ with respect to [100] in the (*hk*0) plane: (a) $\delta = 12.6°$, (b) $\delta = 30.2°$. The ordinate is the absolute photoelectron count rate in counts per second per channel (cnt/s/ch) of the multichannel analyzer. The dots are the accumulated signal. The lines are computer generated smoothed curves. L and T refer to Brillouin shifted signal scattered from quasi-longitudinal and quasi-transverse acoustic phonons, respectively. *R* denotes the parasitic elastic scattering at the laser frequency.

Crystallographic [100] and [110] faces were polished on the sample using standard metallographic techniques, ending with a 0.05-μm abrasive. The orientation was measured to 0.1° in an X-ray goniometer. By changing the angle of incidence of the light, it was possible to vary appreciably the probed phonon direction, **q**, in the (*hk*0) plane. The reference angle δ formed between **q** and [100] was computed from Eq. (1). Observation of either or both of the quasi-longitudinal, L, and quasi-transverse, T, acoustic phonons for which the atomic displacements were in the (*hk*0) plane was possible. Selection rules prohibited the observation of the other transverse phonon having displacements in the [001] direction (*7*). Spectra at $\delta = 12.6$ and 30.2° are shown in Fig. 2.

The frequency shifts $\Delta\nu$ were measured using a Brillouin spectrometer which employs a five-pass Fabry–Perot interferometer having a contrast of 10^{10} at 488 nm (*8*).

The Brillouin intensity was determined by the elasto-optic Pockels tensor. The scattering from the transverse acoustic phonons was stronger than from the longitudinal acoustic phonons for most values of δ indicating that the Pockels coefficient p_{44} was much larger than either p_{11} or p_{12}.

The quasi-longitudinal, v_L, and quasi-transverse, v_T, sound velocities were related to the elastic moduli as a function of δ in the

following manner (*9*):

$$\rho v_{\substack{L\\T}}^2 = (c_{11} + c_{44})/2 \pm \tfrac{1}{2}[(c_{11} - c_{44})^2 \cos^2(2\delta) + (c_{12} + c_{44})^2 \sin^2(2\delta)]^{1/2}, \quad (4)$$

where ρ is the density. The pure longitudinal and transverse waves occur for $\delta = 0$, $\mathbf{q}$ [100], and $\delta = 45°$, $\mathbf{q}$ [110]:

$\mathbf{q}$ [100]:	$\mathbf{q}$ [110]:
$v_L = [c_{11}/\rho]^{1/2}$,	$v_L = [(c_{44} + 2c_{44} + c_{12})/2\rho]^{1/2}$,
$v_T = [c_{44}/\rho]^{1/2}$,	$v_T = [(c_{11} - c_{12})/2\rho]^{1/2}$.

(4a)

Thirteen separate velocities deduced from data taken with the laser operating at 100 mW were used to calculate the three elastic constants. The method of analysis was to divide the velocities into three groups. The first group contained the transverse velocities in the range $10 < \delta < 15°$, the second contained the transverse velocities in the range $25 < \delta < 40°$, and the third contained the longitudinal velocities from $25 < \delta < 40°$. From Eq. (4), it is apparent that the first group would be most sensitive to c_{44}; the second and third groups would combine to give c_{11} and c_{12}. By using a velocity from each group and $\rho = 6.92$ g/cm^3, a set of elastic moduli could be found as a solution to Eq. (4a). All combinations were calculated and the many values for each modulus were averaged. These average values were used to plot ρv_L^2 and ρv_T^2 in Fig. 3 which also shows the original data. The average values along with the rms deviation and the effect of a $\pm 2\%$ error in refractive index n are: $c_{11} = 71.7 \pm 3.5 \times 10^{11}$ dynes/cm^2, $c_{44} = 7.11 \pm 11.25 \times 10^{11}$ dynes/cm^2, and $c_{12} = 10.3 \pm 3.4 \times 10^{11}$ dynes/cm^2.

Using this analysis procedure, values for c_{11} and c_{44} are determined accurately. However, the value of c_{12} is very sensitive to experimental error. While we are in disagreement with the absolute values obtained ultrasonically by Pearsall and Coldren (*1*): $c_{11} = (47.9 \pm 1.4) \times 10^{11}$ dynes/cm^2/$c_{44} = (6.1 \pm 0.2) \times 10^{11}$ dynes/cm^2 and $c_{12} = (-0.7 \pm 2.8) \times 10^{11}$ dynes/cm^2, our pictures of the acoustic propagation are similar in that our measure of the anisotropy factor, $2c_{44}/(c_{11} - c_{12})$, is 0.23 whereas the ultrasonic value is 0.25. Tsuda *et al.* (*2*), who obtained values intermediate between those of Pearsall and Coldren and the present investigation, also obtained a similar anisotropy factor of 0.24 at 20°C. It seems likely that this low anisotropy and unusual ratio for the Pockels coefficients are a result of the low packing density and highly directional bonds (*1*).

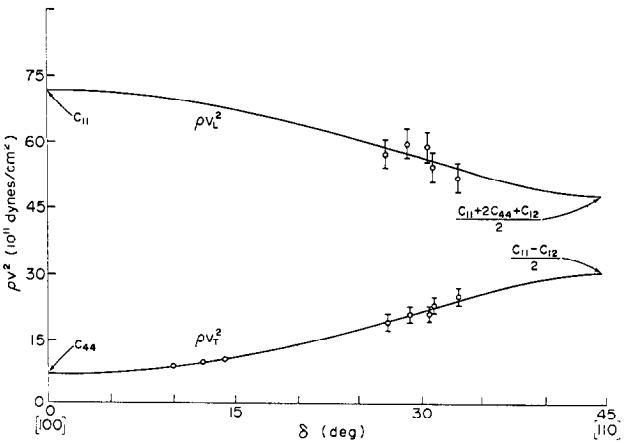

FIG. 3. The variation in the effective elastic modulus as a function of angle δ, the angle between the propagation direction $\mathbf{q}$ and [100] in the ($hk0$) plane. The form for the longitudinal and transverse acoustic phonons, ρv_L^2 and ρv_T^2, was computed using a best fit to the measurements (dots): $c_{11} = 71.7 \times 10^{11}$ dynes/cm^2, $c_{44} = 7.11 \times 10^{11}$ dynes/cm^2, and $c_{12} = 10.3 \times 10^{11}$ dynes/cm^2.

Discussion

Several possible explanations exist for the disagreement between our result, and those obtained from ultrasonic measurements since the Brillouin scattering technique has not previously been applied to solid metals. First is the possibility of systematic error in the Brillouin data acquisition or data reduction. To ensure that the computer programs used in data analysis were applicable to the case of a transparent solid, frequency shifts from longitudinal and transverse thermal acoustic phonons of a pyrex plate were measured in the backscattering geometry. The calculated sound velocities were independent of phonon direction, as expected for an isotropic material, and in agreement with literature values.

The possibility remains that traditional Brillouin scattering theory must be modified to correctly interpret spectra from solids as optically absorbing as ReO_3. The effect of sample opacity on scattering line shapes is currently undergoing active theoretical development. A broadening of Brillouin peaks, which is clearly apparent in the ReO_3 spectra, proportional to the ratio of κ/n has been established (*6*). In addition, theoretical calculations have been made which predict asymmetric line shapes and suggest that the energy of the phonon of wave vector $\mathbf{q}$ should not be associated with the maximum of the Brillouin peak (*10*). Using these alternate formulations with the measured optical indices of ReO_3 indicates no significant deviation of peak maxima. Only if κ^2 is comparable to or greater than n^2 do current theories predict dramatic line shape asymmetries.

The optical constant measurements are also a potential source of error. In the data reduction, one can see from Eqs. (3) and (4a) that the major effect of an error in n would be to cause the same percentage increase or decrease in all measured mode velocities. Although all of our stiffness constant values exceed those obtained by ultrasonics, the ratio of the results of the two techniques varies with modulus. It is 1.51 for c_{11} and 1.15 for c_{44}.

Analysis of our data suggests, however, that the primary cause of the discrepancy between ultrasonics and Brillouin scattering methods is that the measurements are made at different effective sample temperatures. Undoubtedly, a laser operating at 100 mW and focused to a spot having a radius of approximately 10 μm causes some heating of the scattering volume. If the sample is optically absorbing and has a low thermal conductivity, the effect can be significant (*11*). A direct calculation is complicated by the absence of thermal conductivity data for ReO_3 at room temperature. However, using the equation given by Carslaw and Jaeger for a heat flux Q incident on a semi-infinite slab (*12*) an estimate of the temperature increase with laser power based on thermal conductivity data for structurally and electronically similar sodium tungsten bronzes (*13*) yields a measurement temperature of 354°K. Further evidence that significant heating occurs was obtained from a second set of ReO_3 spectra taken with 85 mW ($T = 346$°K) of incident laser power. Elastic constants deduced from the second set of measurements were: $c_{11} = (67.6 \pm 2.9) \times 10^{11}$ dynes/cm^2, $c_{44} = (7.20 \pm .34) \times 10^{11}$ dynes/cm^2, and $c_{12} = (6.4 \pm 2.5) \times 10^{11}$ dynes/cm^2. Further decrease in power was impractical because of the decreased signal-to-noise ratio. A linear extrapolation of the values obtained for c_{11}, c_{44}, and c_{12} to 0 mW, 300°K gives reasonable agreement with ultrasonic values (Fig. 4). From the Brillouin data, the value of c_{44} appears to be weakly temperature dependent. The value of c_{12} also appears to have a positive temperature gradient although the large error bars associated with this elastic constant tend to leave the temperature dependence in question. The temperature dependence for c_{11} is consistent with that reported by Pearsall and Coldren, but is in disagreement with the data of Tsuda *et al.*, who report a negative temperature dependence for all three elastic constants.

The positive temperature dependence of the elastic constants that we observe and that Pearsall and Coldren also report, implies a positive temperature dependence of the Debye

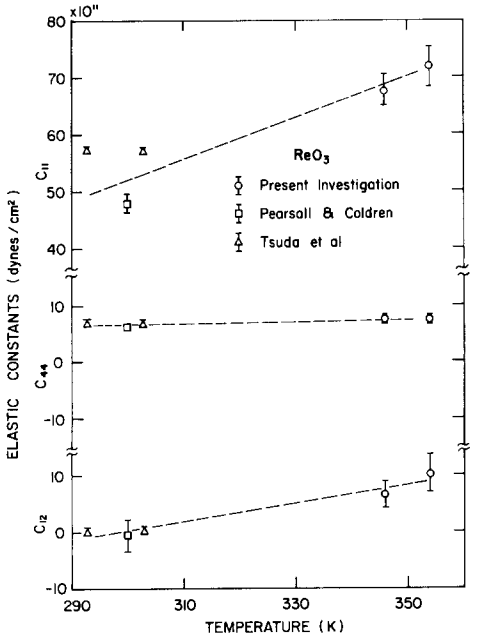

FIG. 4. The elastic constants of ReO_3 as determined in this investigation and as reported by Pearsall and Coldren (*1*) and by Tsuda *et al.* (*2*).

temperature (Θ_D) as well. Pearsall and Coldren and Tsuda *et al.* calculate values for Θ_D at room temperature which are much higher than those reported by Zumsteg and Pearsall (*14*) from low temperature heat capacity measurements of ReO_3. The data of Tsuda *et al.* with a negative temperature dependence depart even further from the heat capacity results at low temperatures. Following Pearsall and Coldren, we calculate a value of 560°K for Θ_D. Our results and those of Pearsall and Coldren are consistent with the temperature dependence of Θ_D reported for $Na_{0.7}WO_3$ near room temperature by Gerstein *et al.* (*15*).

In conclusion, we have shown that Brillouin light scattering is a satisfactory method for the determination of elastic constants of small metal crystals if local heating is taken into account. The results for ReO_3 show a positive temperature dependence of the elastic constants at room temperature and yield Θ_D values considerably higher than those obtained from low temperature heat capacity measurements.

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