

## Brief Reports

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### Room-temperature elastic constants of Sc and ScD<sub>0.18</sub>

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The complete set of elastic constants for Sc and ScD<sub>0.18</sub> has been measured at room temperature. The results show that the addition of hydrogen to this rare-earth metal has a qualitatively different effect than the addition of hydrogen to transition metals such as palladium, vanadium, niobium, and tantalum. In the case of Sc all five elastic constants increase with the addition of hydrogen. The bulk modulus for ScD<sub>0.18</sub> is 9.5% higher than that for Sc. The Debye temperature computed from the room-temperature elastic constants is 355 K for Sc and 371 K for ScD<sub>0.18</sub>.

Many of the rare-earth metals have the ability to absorb large quantities of hydrogen, or deuterium, while retaining the hcp crystal structure. The resulting unusual thermodynamic, structural and dynamic properties of these  $\alpha$ -phase, metal-hydrogen systems,  $RH(D)_x$  ( $R = \text{Sc, Y, Ho, Er, Tm, Lu}$ ), have been the subject of numerous investigations. There is a broad  $\alpha$  phase with  $x$  extending as high as 0.33, down to the lowest temperatures, with no precipitation of the hydride phase.<sup>1</sup> The unusually broad  $\alpha$  phase is connected with considerable ordering of the hydrogen on the tetrahedral sites of the hcp lattice. This ordering was first revealed by resistivity anomalies<sup>2</sup> and later observed by neutron-scattering experiments.<sup>3,4</sup> There is rapid motion of the hydrogen ions among the tetrahedral sites. This motion has been studied by neutron scattering,<sup>5</sup> NMR,<sup>6</sup> internal friction,<sup>7</sup> and ultrasound.<sup>8,9</sup>

While numerous properties of the rare-earth metal-hydrogen systems have been studied, there appear to be no measurements of the elastic constants of these materials, although elastic constants for some of the pure metals have been measured.<sup>10-12</sup> The elastic constants, being the second derivatives of the free energy with respect to strain, are of fundamental importance. In some cases elastic constants can now be calculated from first principles.<sup>13</sup> Experimental values of elastic constants are needed for comparison with theoretical results, and for the calculation of many thermodynamic properties of metal-hydrogen materials. Finally, elastic constants are connected to thermal properties through the Debye theory.

We report here the complete set of second-order elastic constants for Sc and ScD<sub>0.18</sub> measured at a temperature of 303 K. The scandium single crystals were grown at

the Ames Laboratory, Iowa State University from high-purity materials. Rectangular parallelepipeds,  $\approx 2$  mm on an edge, were cut from larger single-crystal samples using an electric discharge machine. After cutting, the samples were lightly electropolished in a methanol-3% perchloric acid solution. Deuterium was loaded from the gas phase as described by others<sup>14</sup> and the amount absorbed was determined from the weight gain. Results are reported below for two samples: Sc and ScD<sub>0.18</sub>. The room-temperature dimensions of these two samples in mm are, respectively,  $1.80 \times 1.89 \times 2.36$  and  $1.51 \times 1.77 \times 2.00$ . In each case, one axis of the parallelepiped was parallel to the crystalline  $c$  axis to within  $0.5^\circ$ , as determined by x-ray diffraction. For Sc the axis of the parallelepiped aligned along the  $c$  axis was the short axis whereas for ScD<sub>0.18</sub> it was the long axis. Because a crystal of hexagonal symmetry is elastically isotropic in the basal plane, the orientations of the other crystalline axes relative to the parallelepiped were not determined.

Resonant ultrasound spectroscopy<sup>15</sup> was used to measure the elastic constants. With this technique a single-crystal rectangular-parallelepiped sample is placed corner-to-corner between two piezoelectric transducers; one transducer is used for the generation and the other for the detection of ultrasonic vibrations. By sweeping the excitation frequency, a large number of the lowest-frequency vibrational eigenmodes of the sample can be measured. From such a spectrum of eigenfrequencies a complete set of elastic constants can be determined. We measured over 40 resonances for each of the samples.

A segment of the frequency spectrum for a ScD<sub>0.18</sub>, single-crystal, parallelepiped is shown in Fig. 1. Seven

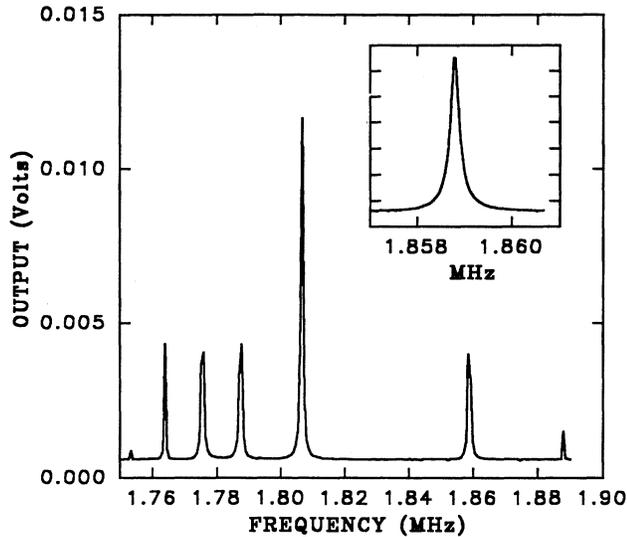


FIG. 1. Resonant-ultrasound spectrometer output for a  $\text{ScD}_{0.18}$  single-crystal rectangular parallelepiped showing seven eigenfrequencies. The inset shows one of the resonant frequencies in greater detail. Sample dimensions  $1.86 \text{ mm} \times 2.35 \text{ mm} \times 1.78 \text{ mm}$ . The long axis of the parallelepiped was parallel to the crystalline  $c$  axis.

resonances are shown in the main figure and the inset shows one of the resonances in more detail. For this material, the  $Q$ 's of the lines were on the order of  $10^4$  so that a precise determination of the eigenfrequencies was possible. The elastic constants were determined from the measured eigenfrequencies using the method of Visscher *et al.*<sup>16</sup> The density and sample dimensions are also needed to calculate the elastic constants. We computed the density from the atomic masses and the lattice parameters of Sc and  $\text{ScD}_{0.33}$ , which have been accurately determined by neutron scattering.<sup>17</sup> For our sample with a deuterium concentration of  $x=0.18$  we used a linear interpolation of the results at  $x=0$  and  $0.33$ . The resultant values of density were  $\rho(\text{Sc})=2.989 \text{ gm/cm}^3$  and  $\rho(\text{ScD}_{0.18})=2.975 \text{ gm/cm}^3$ . The sample dimensions also enter into the calculations. For the small, soft samples we used, it is much easier to obtain an accurate measurement of the mass than of the sample dimensions. If the mass and density are known, then obviously the product of the three orthogonal dimensions,  $abc$ , is also known, but the ratios,  $a:b:c$ , are not. We used the mass and the known density to determine the product  $abc$ . We made an approximate measurement of the dimensions which we used as starting values for the calculation of the elastic constants, but left the ratios as a parameter used in fitting the data. For Sc we fit 40 frequencies with a rms deviation of 0.31%; for  $\text{ScD}_{0.18}$  we fit 41 frequencies with a rms deviation of 0.43%. The present values of elastic constants, along with the previously<sup>12</sup> measured values for Sc, are presented in Table I.

Two points are apparent from Table I. First, the agreement between the present results for Sc and those of Ref. 12 is excellent, the average difference being less than 0.6%. The results of Ref. 12 were obtained using conven-

TABLE I. Elastic constants, in units of  $10^{11}$  Pa, for Sc and  $\text{ScD}_{0.18}$  measured at 303 K.

	$C_{11}$	$C_{33}$	$C_{13}$	$C_{44}$	$C_{66}$
$\text{ScD}_{0.18}$	1.078	1.151	0.320	0.313	0.287
Sc	0.986	1.062	0.295	0.275	0.269
Sc (Ref. 12)	0.993	1.069	0.294	0.277	0.268

tional ultrasonic techniques while the present results were obtained using resonant ultrasound spectroscopy. Second, all the elastic constants increase with the addition of deuterium. We have made less extensive measurements of  $\text{ScH}_{0.25}$ . Those results also indicated an increase of the elastic constants with the addition of hydrogen. The results are consistent with an isotope-independent linear increase of elastic constants with hydrogen concentration.

Using the results of Table I we calculate the bulk modulus, which for a crystal of hexagonal symmetry is given by

$$B = \frac{C_{33}(C_{11} - C_{66}) - C_{13}^2}{C_{11} + C_{33} - C_{66} - 2C_{13}} \quad (1)$$

The values are given in Table II. Also given in Table II are Cauchy ratios for hexagonal crystals. Under certain conditions the Cauchy relations hold for the elastic constants. These conditions are (1) the interatomic interactions are described by central forces; (2) each lattice site is an inversion center; and, (3) there are no initial stresses. For hexagonal symmetry these relations take the form<sup>18</sup>  $C_{13}/C_{44}=1$  and  $C_{11}/(3C_{66})=1$ .

Finally, we calculate the Debye temperature from the room-temperature elastic constants. The calculation involves an average of the three independent sound velocities over all directions. The sound velocities as a function of direction may be calculated from the measured elastic constants. The calculation simplifies considerably in the case of hexagonal symmetry due to the elastic isotropy in the basal plane. In this case it is only necessary to average over  $0 \leq \alpha \leq \pi/2$ , where  $\alpha$  is the angle between the propagation direction and the hexagonal axis. The Debye temperature  $\Theta_D$  is given by<sup>19</sup>

$$\Theta_D = \frac{(h/k_B)[(9/4\pi)(N/V)]^{1/3}}{\left[ \int_0^{\pi/2} (1/v_1^3 + 1/v_2^3 + 1/v_3^3) \sin \alpha d\alpha \right]^{1/3}}, \quad (2)$$

where  $h$  is Planck's constant,  $k_B$  is Boltzmann's constant,  $N/V$  is the number of Sc atoms per volume, and the  $v_i$  are the three independent sound velocities for each direction. Expressions for  $v_i$  in terms of the elastic constants, the sample density, and the angle  $\alpha$  have been given by Musgrave.<sup>20</sup> Values of  $\Theta_D$  computed in this manner

TABLE II. Bulk modulus, Debye temperature, and Cauchy ratios at 303 K calculated from the present measurements.

	$B$ ( $10^{11}$ Pa)	$\Theta_D$ (K)	$C_{13}/C_{44}$	$C_{11}/(3C_{66})$
$\text{ScD}_{0.18}$	0.621	371	1.02	1.25
Sc	0.567	355	1.07	1.22

from the present data are given in Table II. The values of  $\Theta_D$  shown in Table II would be expected to increase slightly if computed from elastic constants measured near 0 K because the lattice stiffens with decreasing temperature. A computation of  $\Theta_D$  for Sc from the elastic constants at 4.2 K reported in Ref. 12 gives 361 K, in excellent agreement with the value of 359.5 K determined from specific-heat measurements<sup>21</sup> near 0 K.

Tables I and II show unusual features in comparison with other metal hydrogen systems. All the elastic constants *increase* with the addition of deuterium. The bulk modulus *increases* by 9.5% with the addition of deuterium to  $x = 0.18$  while the Debye temperature increases by 4.7%. The Cauchy relations are not strongly violated. These results will now be compared to the behavior of other metal-hydrogen systems.

The elastic constants of the fcc palladium-hydrogen system have been the subject of several studies.<sup>22-28</sup> The bulk modulus of this system *decreases* about 6% with the addition of hydrogen or deuterium to  $x \approx 0.7$  while the Debye temperature increases about 1.6%. The decrease in the bulk modulus is a result of a decrease in the elastic constants  $C_L = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$  and  $C_{44}$ , but an increase in the shear constant  $C' = \frac{1}{2}(C_{11} - C_{12})$ . The Cauchy condition is strongly violated with  $C_{12}/C_{44} \approx 2.5$ . The situation was found to be somewhat different for a Pd<sub>0.85</sub>Pt<sub>0.15</sub> single crystal.<sup>29</sup> The measured shear elastic constants of this material decrease strongly with hydrogenation (3-20% decrease for  $x = 0.29$ ), but the behavior of the longitudinal modes is more complicated: the result is that hydrogenation causes the bulk modulus to decrease by about 1% at room temperature, and to increase by about 2% at 20 K.

The elastic constants of the bcc transition metals vanadium, niobium, and tantalum containing hydrogen have also been studied. Measurements on single crystals of these materials at room temperature revealed that  $C'$  decreases with the addition of hydrogen,  $C_{44}$  increases, and the bulk modulus remains nearly constant for hydrogen concentrations of a few atomic percent.<sup>30</sup> An extensive study<sup>31,32</sup> of the Nb-H(D) system at higher temperatures and higher hydrogen concentrations showed that  $C'$  and  $C_{11}$  decrease while  $C_L$ ,  $C_{44}$ , and the bulk modulus increases with increasing H(D) content. At 528 K the bulk modulus increases 4.2% for H/Nb=0.7. For Nb-V and Nb-Ta alloys,<sup>33</sup> room-temperature measurements show that  $C_{11}$  and  $C'$  decrease with the addition of hydrogen while  $C_{44}$  increases. The result is that the bulk modulus of Nb<sub>32</sub>Ta<sub>68</sub> increases about 2.6% for  $x = 0.46$  whereas the bulk modulus of Nb<sub>18</sub>V<sub>82</sub> shows little change.

The above brief survey shows that hcp Sc behaves qualitatively differently with the addition of hydrogen as compared to the fcc Pd system or to the bcc V, Nb, and Ta systems. For Sc all the elastic constants increase with the addition of hydrogen and so does also the bulk modulus. The dependence of the bulk modulus on concentration of hydrogen is considerably stronger for Sc than for the other metal-hydrogen systems surveyed. The stiffening of the elastic properties of scandium with the addition of hydrogen is in qualitative agreement with inelastic-neutron-scattering measurements,<sup>34</sup> and must be regarded as another unusual feature of the rare-earth metal-hydrogen materials.

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