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2009 J. Phys. D: Appl. Phys. 42 095414

(http://iopscience.iop.org/0022-3727/42/9/095414)

J. Phys. D: Appl. Phys. **42** (2009) 095414 (4pp) doi:10.1088/0022-3727/42/9/095414

Elastic moduli of superhard rhenium diboride

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Received 9 February 2009, in final form 13 March 2009
Published 16 April 2009
Online at stacks.iop.org/JPhysD/42/095414

Abstract
The elastic moduli of polycrystalline rhenium diboride are measured as a function of temperature between 5 and 325 K. The room temperature results show that ReB_2 has very high values for both the bulk and shear modulus, confirming the incompressible and superhard nature of this material. With decreasing temperature, the moduli increase, with a hint of softening below 50 K.

The search for superhard materials, indispensable for industrial applications such as scratch-resistant coatings and cutting tools, has recently led to the identification of rhenium diboride (ReB_2) as a potential superhard and incompressible solid. Although the synthesis at ambient pressure was established in 1962 [1] its scientifically interesting mechanical properties were revealed only recently, through hardness and incompressibility measurements [2], reporting a maximum hardness of 55.5 GPa under a load of 0.49 N. Since the hardness is deduced from the size of the indentation after deformation, a hard material typically requires a high bulk modulus (in order for the material to support the volume decrease created by the applied pressure), and a low Poisson ratio or high shear modulus (such that the material will not deform in a direction different from the applied load), and the materials must have minimal plastic deformation [3]. Diamond, the archetypal hard material, has a bulk modulus of 443 GPa (the record incompressibility until the bulk modulus of osmium was measured to be 462 GPa) [4], and a Poisson ratio of 0.08. Because of the strong correlation between the hardness of a material and its elastic moduli, multiple theoretical studies of ReB_2 have focused on the calculation of its elastic moduli, predicting values of the shear modulus in the range 290–310 GPa, and values of the bulk modulus between 340 and 370 GPa [5–12]. However, experimental studies of the elastic moduli have thus far not been reported. In this paper, we present the elastic moduli for polycrystalline ReB_2, measured using resonant ultrasound spectroscopy (RUS) [13–16] as a function of temperature between 5 and 325 K.

A polycrystalline ingot of ReB_2 was synthesized by arc melting the appropriate amounts of Re (99.9%) and B^{11} (99.9%) in an Ar atmosphere. Coarse powders of the elements were first mixed together and then pressed into a pellet with an initial composition of $ReB_{2.5}$. The pellet was arc-melted on a water-cooled copper hearth and flipped 6–7 times to ensure chemical homogeneity. Assuming only B is lost during the melting process, the final weight of the ingot corresponded to a composition of ReB_2. To confirm the phase purity of the obtained sample, powder x-ray spectroscopy was performed. As is shown in figure 1, the diffraction pattern for our sample matches that of ReB_2, confirming successful synthesis under atmospheric pressure and the absence of significant impurities. All lines in the pattern can be indexed using a hexagonal unit cell with $a = 2.8998(2)$ Å and $c = 7.4763(8)$ Å. Three specimens of approximately $2 \times 2.5 \times 3\,mm^3$ were cut out of the sample and prepared for RUS measurements. RUS is based on the measurement of the resonances of a freely vibrating body [13–16]. Whereas the mechanical resonances can be calculated for a sample with known dimensions, density and elastic tensor, RUS uses an inverse procedure, in which the mechanical resonances of a freely vibrating solid of known shape are measured, and an iteration procedure is used to 'match' the measured lines with the calculated spectrum. RUS allows the determination of all elastic constants of the solid from a single frequency scan, which gives the technique a clear advantage over more conventional methods: there is no need for separate measurements to probe different moduli. RUS also eliminates the need for bonding agents, as the sample is lightly held between two transducers. Another advantage lies in the ability of RUS to work with small samples: whereas conventional techniques can demand a sample size up to a centimetre, RUS measurements can be made on millimetres-sized samples. The RUS data reported here were carried out

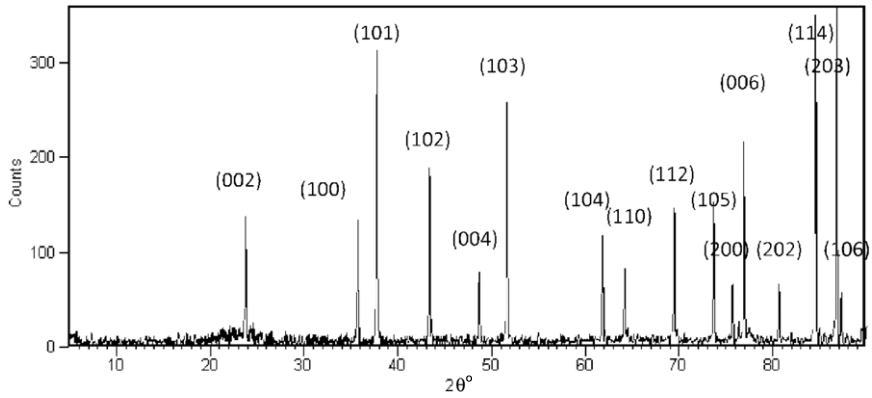

Figure 1. Observed x-ray pattern for polycrystalline ReB_2. All lines in the pattern are indexed using a hexagonal unit cell with $a = 2.8998(2)$ Å and $c = 7.4763(8)$ Å.

Table 1. Measured bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio σ and Debye temperature θ_D of ReB_2 compared with theoretical data reported by others.

	L (GPa)	G (GPa)	B (GPa)	E (GPa)	σ	θ_D (K)
Experiment						
300 K	685	276	317	642	0.163	738
5 K	693	280	320	650	0.161	738
Hao [5, 7]						
LDA	762.4	294.9	369.2	698.7	0.1846	
GGA	750.4	289.4	364.5	682.5	0.1791	
	695	264	343	630	0.1937	716
Wang [6]						
LDA	776	313	359	696	0.22	
GGA	749	304	344	642	0.21	774
Liang [9]						
LDA	772	310	359	725	0.171	782
	763[a]	305[a]	356[a]	714[a]	0.172[a]	
Zhou [10]						
GGA	727	283	350	669	0.182	749

[a] These calculations include spin–orbit coupling in Re.

as a function of temperature using a custom designed probe that was inserted in a commercial quantum design physical properties measurement system (PPMS).

Polycrystalline materials are elastically isotropic, i.e. they have only two independent elastic moduli. Whereas the bulk modulus B (with the strains perpendicular to the stress directions all equal) and the shear modulus G (with the strains perpendicular to the stress directions all zero) are usually considered the fundamental moduli for isotropic solids [17], acoustic measurements will yield the longitudinal modulus L and the shear modulus G, which are directly linked to the longitudinal and transverse sound velocities, v_L and v_T, in the material: $v_L = (L/\rho)^{1/2}$ and $v_T = (G/\rho)^{1/2}$. The bulk modulus (B), Young's modulus (E) and Poisson's ratio (σ) are connected to L and G through the following relations [17]:

$$B = \frac{3L - 4G}{3}, \tag{1}$$

$$E = \frac{G(3L - 4G)}{L - G}, \tag{2}$$

$$\sigma = \frac{L - 2G}{2(L - G)}. \tag{3}$$

Table 1 lists the values for the elastic moduli obtained at room temperature and at 5 K using RUS. For comparison, the table also includes reported calculated moduli, using the generalized gradient approximation (GGA) and the local density approximation (LDA) for single crystals. Whereas these theoretical calculations yield the moduli for single crystals, values for polycrystals can be estimated using the Reuss–Voigt–Hill averaging scheme [18], and the moduli in the table are the Hill averages of the calculated single crystal moduli. Our experimental values show excellent agreement with the theoretical values, as well as the bulk modulus reported by Chung *et al* [2], obtained from compressibility methods. The table also lists the Debye temperature, which is obtained using [17]

$$\theta_D = \frac{h}{k_B}\left(\frac{9N_A\rho}{4\pi(M/p)}\right)^{1/3}\left[\frac{2}{v_T^3} + \frac{1}{v_L^3}\right]^{-1/3}, \tag{4}$$

where h, k_B and N_A are Planck's constant, the Boltzmann constant and Avogadro's number, respectively, M/p is the molecular weight divided by the number of atoms per formula unit, ρ is the density and v_T and v_L are the transverse and longitudinal velocities. Again, excellent agreement is reached between the Debye temperature derived from our experimental data and the theoretical predictions.

Figures 2 and 3 show the temperature dependence of the elastic moduli L and G for ReB_2. A gradual stiffening of the

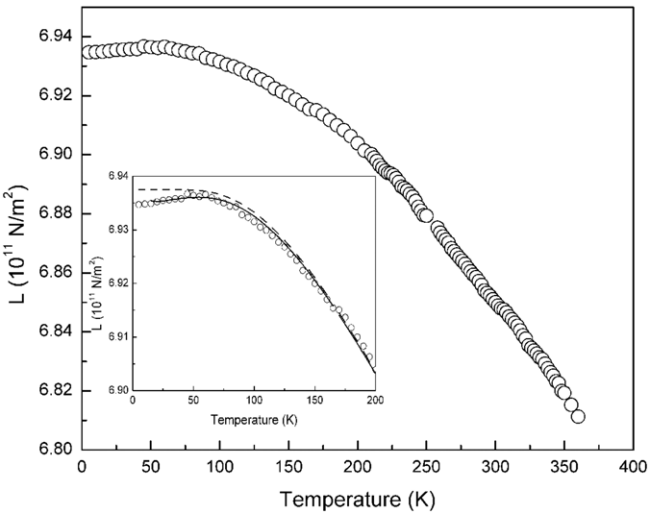

Figure 2. Temperature-dependence of the longitudinal modulus of ReB_2. Inset: model calculation using a TLS with spacing $\Delta = 30$ K. The dashed line is the estimated Varshni background (with parameters $s = 0.205 \times 10^{11}$ N m^{-2} and $t = 390$ K), the solid line through the data includes the contribution of the TLS.

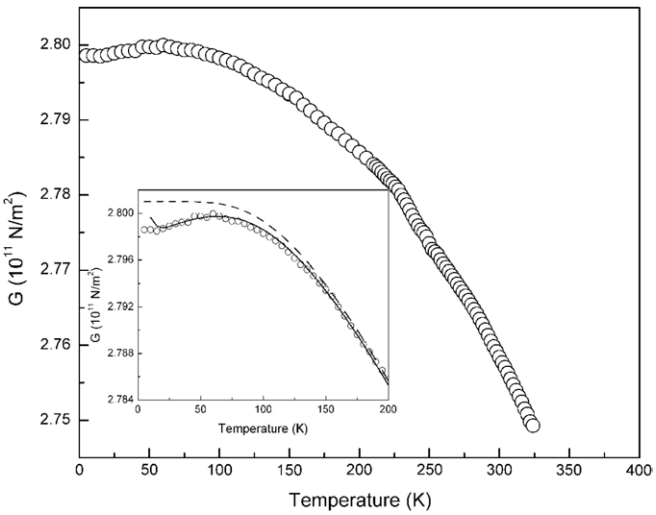

Figure 3. Temperature-dependence of the shear modulus of ReB_2. Inset: model calculation using a TLS with spacing $\Delta = 30$ K. The dashed line is the estimated Varshni background (with parameters $s = 0.110 \times 10^{11}$ N m^{-2} and $t = 420$ K), the solid line through the data includes the contribution of the TLS.

moduli with decreasing temperature is observed, levelling-off at low temperatures. This is known as the so-called Varshni behaviour [19], after Varshni who modelled the temperature dependence of over 20 compounds with the empirical formula $c_{ij}(T) = c_{ij}^0 - s/(\mathrm{e}^{t/T} - 1)$, with T the temperature, c_{ij}^0 the elastic constant at 0 K and s and t fitting parameters. This function was shown by Varshni to describe the temperature dependence of the elastic constants of many simple substances and characterizes to some extent 'normal' elastic behaviour. Close inspection of the temperature dependence of our elastic data shows that ReB_2 somewhat deviates from the normal Varshni behaviour: the elastic moduli show a slight but significant drop below 50 K, where normal elastic behaviour

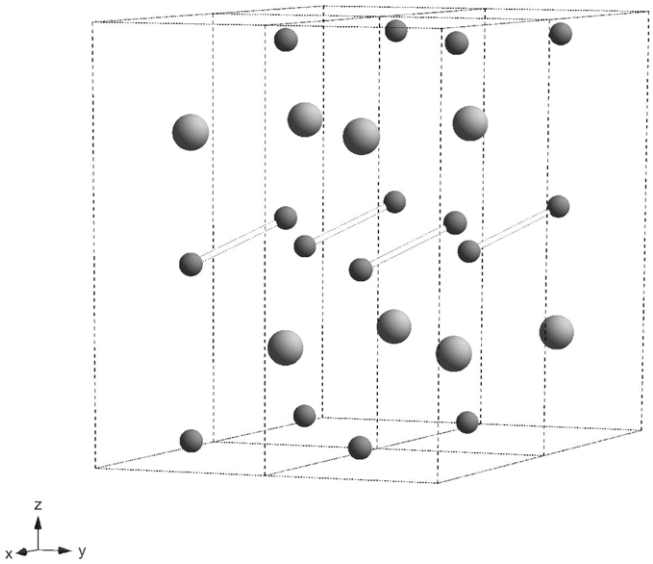

Figure 4. Crystal structure of ReB_2. The Re atoms are presented as big spheres, the B atoms as small spheres. The strong B–B bond is also plotted.

would be levelling-off to a temperature-independent regime. Such a softening has been observed in metallic glasses [20, 21] and intermetallic compounds that contain loosely bound atoms that 'rattle' in an oversized atomic cage [22–24], and has been described by taking into account the elastic response of a local oscillator with an Einstein or two-level character. The contribution of a two-level system (TLS) to the elastic response can be calculated from $c = \partial^2 F/\partial\varepsilon^2$ with $F = -N_A k_B T \ln(1 + \mathrm{e}^{-\Delta/T})$ the Helmholtz free energy of a TLS, and assuming that the vibrational level spacing, Δ, depends linearly on the strain, ϵ, that is, $\Delta = \Delta_0 + A\epsilon$, with A a coupling constant. The insets of figures 2 and 3 illustrate that the observed decrease in the ReB_2 moduli at low temperatures can indeed be adequately modelled by adding the elastic response of a TLS with level spacing $\Delta = 3$ K to a 'background' contribution estimated from the Varshni equation. The physical origin of such a local mode in superhard ReB_2 is quite puzzling. The structure of ReB_2, shown in figure 4, does not reveal an obvious site for potential rattlers. Due to the low frequency that characterizes the observed mode, it is tempting to attribute it to the heavier Re atom. ReB_2 does indeed stand out for its combination of very light (B, $A = 10.811$ g mol^{-1}) and very heavy (Re, $A = 186.207$ g mol^{-1}) atoms, and the latter are expected to dominate the low-energy lattice dynamics of this material. Heavy atoms have been known to be prone to rattling, as was, for instance, illustrated by the case of LaB_6, where the heavier La atom was found to be the source of a localized rattler mode [23]. An alternative explanation for the observed soft mode could be found in the B–B dumbbells, illustrated in figure 4. Neutron scattering experiments on Zn_4Sb_3 by Schweika *et al* revealed local soft and strongly anharmonic modes of Sb dimers that dominate and drive the dynamic response of this material [25]. It is not implausible that the strong covalent B–B bond [10] in ReB_2 results in 'B–B dumbbell rattlers', responsible for the observed soft mode. Determination of the atomic displacement

parameters of ReB_2 might be able to provide further insight into the dynamics of the constituent atoms.

In summary, the elastic measurements reported in this paper provide experimental evidence for the high elastic moduli that have been theoretically predicted for ReB_2. The temperature dependence of both the longitudinal and shear modulus shows a gradual stiffening with decreasing temperature, but displays a hint of softening below 50 K, suggesting that the lattice dynamics of superhard ReB_2 deviates from normal behaviour.

Acknowledgments

We thank Dr J Spruiell for his help with the x-ray measurements and analysis. Work at The University of Tennessee is supported by NSF grant DMR-0804719. Research at Oak Ridge is sponsored by the Division of Materials Science and Engineering, Office of Basic Sciences, US Department of Energy.

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