

Elastic moduli of polycrystalline ZrCo as a function of temperature

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Abstract

The polycrystalline elastic moduli of the intermetallic compound ZrCo have been measured over the temperature range of 3–410 K. The temperature dependence of the moduli resembles that of ordinary metals; the moduli approach zero temperature with zero slope, but decrease monotonically with increasing temperature at higher temperatures. The 296 K values of the bulk, shear, and Young's moduli are, respectively, 140, 49.2, and 132 GPa. Poisson's ratio is almost temperature-independent increasing from 0.338 at low temperatures to 0.343 at 410 K. The acoustic contribution to the low temperature specific heat, calculated from the elastic moduli measured at 3 K, is 9.32×10^{-5} J/(mol K⁴). The corresponding Debye temperature is 347 K.

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1. Introduction

The intermetallic compound ZrCo has received considerable attention as a favorable material for the storage and release of hydrogen isotopes [1–4] due to its ability to store large amounts of hydrogen combined with its low hydrogen equilibrium pressure [5]. Various thermodynamic [6] and kinetic [7–9] studies have been carried out on the ZrCoH_x system. The hydrogen dissociation pressure is not far from that of uranium [1], which has led to ZrCo being selected for hydrogen isotope storage and recovery by the international thermonuclear experimental reactor team [10]. The compound is of particular interest for the storage of tritium [11]. This material has been investigated by X-ray [9,12] and neutron [13–15] techniques. Both ZrCo and the low hydrogen concentration α phase of ZrCoH_x were shown to possess the cubic, CsCl, structure. The electronic structure of ZrCo and its hydride have been investigated theoretically [16] and it was found that Zr–H interactions play a crucial role in the stability of the hydride.

Although ZrCo has been studied by a variety of methods due to its technological importance, there appear to be few reports of the mechanical properties of this material. In particular, no measurements of the elastic moduli have

been reported. A knowledge of the elastic constants is important for a variety of reasons. At the most fundamental level the adiabatic elastic constants are given by the second derivatives of the internal energy with respect to strain and thus are related to interatomic potentials. They are also related to the thermal properties of a solid through the Debye theory. More specifically for metal-hydride materials, the elastic constants are useful for an evaluation of the elastic contribution to the hydrogen–hydrogen interaction energy [17] and the elastic energy associated with the precipitation of hydride phases [18,19]. The present paper reports the ultrasonic measurement of the elastic moduli of polycrystalline ZrCo over the temperature range of 3–410 K. Various parameters derived from the measurements are also presented.

2. Experimental

The elastic moduli were measured using the technique of Resonant Ultrasound Spectroscopy (RUS) [20–22]. The measurements were made with a commercial spectrometer (Dynamic Resonance Systems). With the RUS technique, piezoelectric transducers are used to excite a large number of the lowest frequency vibrational eigenmodes for samples of well-defined shapes, such as rectangular parallelepipeds. The ZrCo ingot was prepared by arc-melting together equimolar amounts of zirconium and cobalt as

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described previously [7]. Ref. [7] gives details of the chemical, X-ray, and metallurgical analysis. For the present study, a low-speed diamond saw was used to cut an approximate parallelepiped from the same ingot used for the previous work [7]. This sample was then hand polished into an accurate rectangular parallelepiped suitable for the ultrasonic measurements. The edge dimensions of the sample were 2.186 mm, 1.671 mm, and 0.781 mm. Figure 1 shows a section of an RUS spectrum for the ZrCo sample taken at 100 K. Three resonances are shown. The clean spectrum and narrow lines are an indication of the high quality of the sample. The elastic constants are calculated from the measured frequencies by an iterative procedure [23,24]. For the entire temperature range investigated, the frequencies of the lowest 20 resonances were measured with a typical rms difference between measured and computed frequencies of 0.20%. For materials with isotropic symmetry, only two independent moduli are required to fully define the elasticity of the system. The aggregate elastic moduli C_{11} and C_{44} were derived directly from the measured frequencies. C_{44} is simply the usual polycrystalline shear modulus $G(T)$. The temperature-dependent measurements below room temperature were made using either a commercial ^4He cryostat or a home-built gas flow cryostat, and temperature controller. Measurements above room temperature were made using a commercial oven. The temperature was measured with a calibrated silicon diode thermometer.

The room temperature density, calculated directly from the sample dimensions and mass, was 7.573 g/cm^3 . The theoretical density calculated from the published lattice constant [8] of 0.3201 nm is 7.600 g/cm^3 representing a difference of 0.35%, well within the measurement error. Errors in the mass density result in comparable errors in the absolute values of the elastic moduli derived from the measured resonant frequencies. Taking into account both the rms error in the RUS fit and that estimated for the

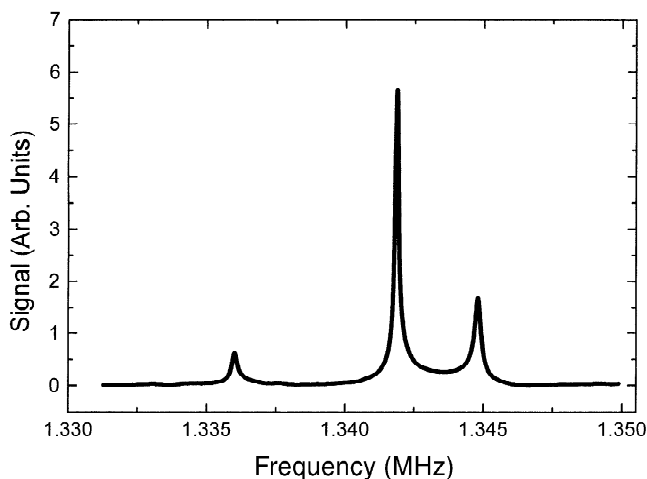


Fig. 1. Section of an RUS spectrum for ZrCo at 100 K showing three resonances.

density measurement, the resulting overall error in the absolute values of the moduli were estimated. These errors are represented as error bars on the graphs presented below. The relative error is, of course, much smaller and is essentially indicated by the scatter in the data.

3. Results and discussion

As mentioned above, 20 resonances were investigated over the temperature range of 3–410 K. Although the primary objective was to use the resonant frequencies to determine the elastic moduli, the Q -values of some of the resonances were measured to derive the ultrasonic loss. The loss in the prepared ZrCo sample is low with a typical value of $Q^{-1} \approx 2 \times 10^{-4}$ and is essentially temperature-independent below 240 K. Above 240 K the loss begins to increase with increasing temperature, probably due to the interaction of the ultrasound with thermal phonons.

Figure 2(a) shows the bulk modulus, calculated from C_{11} and C_{44} mentioned above, over the temperature range of 3–410 K. Figure 2(b) shows the aggregate shear modulus ($G=C_{44}$) over the same temperature range. Because thermal expansion data are presently not available for ZrCo the results have not been corrected for thermal contraction; the room temperature dimensions and density were used in the analysis. The sample dimensions and density are needed to calculate the elastic constants deduced from the measured frequencies. Taking into account the direct dimensional effects as well as the indirect effect through the density, the computed C_{ij} vary inversely with the dimensions. Materials such as Zr and Co have a total thermal contraction of less than 0.2% on cooling from room temperature to 3 K [25]. This value is typical of metals and alloys [26]. Furthermore, the thermal expansion of alloys does not seem to differ much from that of the constituent elements. Assuming that ZrCo behaves similarly, then correcting for thermal contraction would add at most 0.2%, i.e. $\approx 0.3 \text{ GPa}$, to the bulk modulus at 3 K. Similar considerations indicated that the bulk modulus at 410 K would be 0.2% ($\approx 0.3 \text{ GPa}$) lower than the value shown in Fig. 2(a). Comparable percentage considerations apply to the other moduli to be presented below. Overall, the neglect of thermal expansion has a very minor effect on the results.

The temperature (T) dependence of the elastic constants is directly related to the anharmonic nature of the lattice vibrations. The lattice vibrations typically contribute a T^4 term to the internal energy at low temperatures and a term linear in temperature at higher temperatures [27]. In metals there is also a contribution to the internal energy from the conduction electrons, which for simple metals results in a T^2 term at low temperatures [28]. As mentioned above, the adiabatic elastic constants are given by the second derivatives of the internal energy with respect to strain; thus, the temperature dependence of the lattice and electronic energies directly affects the temperature dependence of the

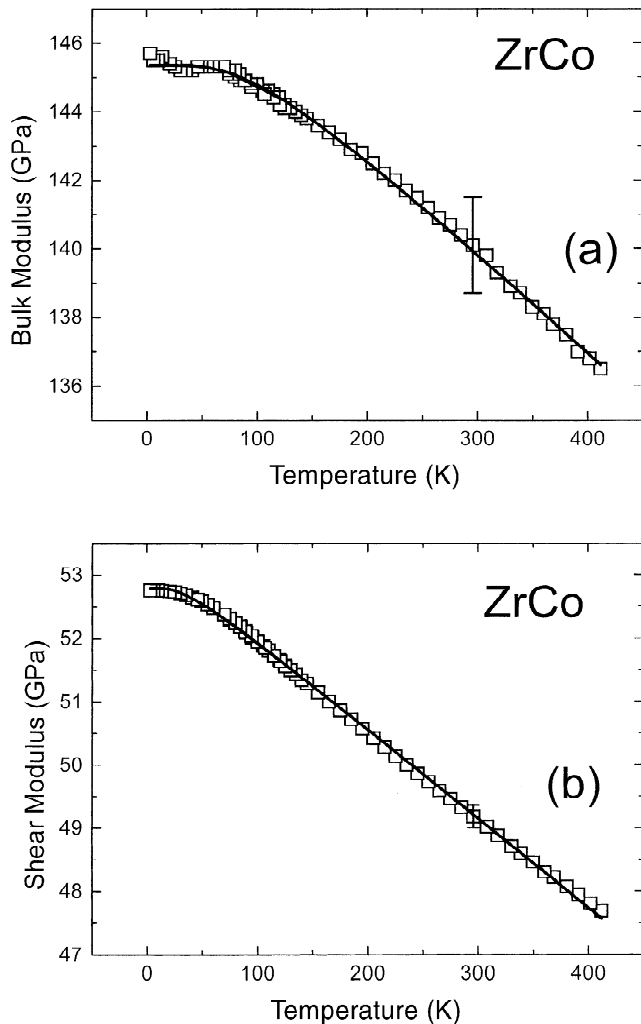


Fig. 2. Elastic moduli of polycrystalline ZrCo versus temperature: (a) Bulk modulus, B ; (b) Shear modulus, G . The small dip in B near 30 K is believed to be an artifact of the fitting procedure, not a real physical effect. The solid lines represent a fit of the semi-empirical Varshni expression to the data. The fitting parameters are given in the text.

C_{ij} . The lattice and electronic energies also contribute to the thermal expansion of the crystalline lattice, which in turn plays a significant role in the temperature dependence of the C_{ij} . The overall result, for typical materials, is that the elastic moduli approach 0 K with zero slope and decrease monotonically with increasing temperature. This simple picture is not applicable to materials undergoing phase transitions [29,30] or to materials with more complicated electronic structures [31–33]. Fig. 2 shows that the moduli of ZrCo behave in a normal fashion, becoming linear in temperature at high temperature. There is an indication of a small anomaly in the bulk modulus around 30 K. We believe this small effect, about 0.3%, is just an artifact of the fitting of the frequencies to find the elastic constants. The bulk modulus is less accurately determined than the shear modulus because few of the lower resonant frequencies depend strongly on C_{11} , whereas the depen-

dence on C_{44} is strong. The resonant frequencies with somewhat stronger dependence on C_{11} did not obviously show the same effect as Fig. 2(a). Also, the loss showed no anomaly near 30 K suggesting that nothing unusual is happening in this temperature range.

The temperature dependence of the elastic constants of many materials is described successfully by the semi-empirical Varshni expression [34,35]

$$C(T) = C(0) - \frac{s}{\exp(t/T) - 1} \quad (1)$$

where $C(0)$, s , and t are three adjustable parameters with $C(0)$ being the value of the elastic constant C at zero temperature. The solid lines in Fig. 2 represent the fit of Eq. (1) to the data for the bulk and shear moduli. The fitting parameters $C(0)$, s , and t for the bulk modulus are 145.3 GPa, 8.2 GPa, and 273 K, respectively. Similarly, these three parameters for the shear modulus are 52.8 GPa, 1.3 GPa, and 92.4 K, respectively. As Fig. 2 shows, this simple expression gives a good account of the temperature dependence of the moduli. This provides additional evidence that the temperature dependence of the polycrystalline elastic moduli of ZrCo resembles that of many other materials.

Although only two independent elastic moduli are required to characterize the elastic behavior of an isotropic solid, other elastic parameters can be easily calculated and can be useful. Fig. 3(a) shows Young's modulus over the temperature range investigated. Like the shear modulus, it decreases almost linearly with temperature above 80 K. Finally, Fig. 3(b) gives Poisson's ratio ν . Poisson's ratio can be defined for a uniaxially stressed rod as the negative ratio of the transverse and longitudinal strains. In polycrystals, ν is bound by 0 and 1/2. A value of 1/2 would correspond to no volume change during deformation. Poisson's ratio increases very slightly with increasing temperature. Both the value of $\nu \approx 0.34$ and the observed temperature dependence are characteristic of metals [35]. The small upturn at low temperatures follows directly from the small anomaly in B shown in Fig. 2(a), and so is not believed to represent a real effect.

It has been found that the bulk modulus of intermetallic compounds can often be estimated as the weighted average of the bulk moduli of the constituent metals [36–38]. Using the reported bulk modulus of Zr [39,40] and Co [40,41] at 298 K of 189.8 and 95.3 GPa, respectively, yields 142.5 GPa as the weighted average value. This value is only 1.8% greater than our measured value of 140.0 GPa for ZrCo at the same temperature. However, such a simple averaging scheme does not produce similarly good results for the shear modulus.

It seems interesting to compare the elastic properties of ZrCo with those of other hydrogen absorbing materials. It has recently been suggested that mechanical properties, particularly ductility, are related to the initial hydriding mechanism [7]. It may be worthwhile to compare the

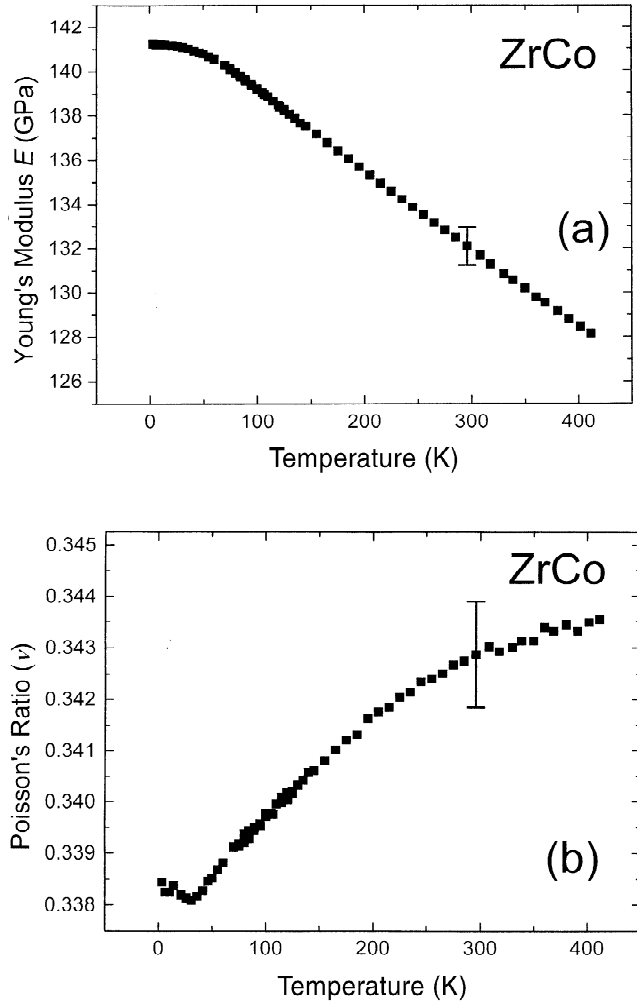


Fig. 3. Elastic parameters of polycrystalline ZrCo versus temperature: (a) Young's modulus, E ; (b) Poisson's ratio, ν . The small upturn at low temperature follows directly from the small dip shown in Fig. 2(a) and is believed to be an artifact of the fitting procedure, not a real physical effect.

elastic properties of various hydrogen-absorbing materials using the present results, recent measurements [42] on LaNi_5 , and literature values [40] for U [43,44], Gd [45], Pd [46], TaV_2 [47], and ZrCr_2 [47]. Table 1 gives the comparison for the bulk, shear, and Young's moduli, as well as Poisson's ratio for these materials. All the results in

Table 1
Comparison of the bulk modulus, B , shear modulus, G , Young's modulus, E and Poisson's ratio, ν , for several hydrogen-absorbing materials

Material	B (GPa)	G (GPa)	E (GPa)	ν
ZrCo	140	49.2	132	0.343
U	113	84	202	0.202
LaNi_5	137.4	59.2	155	0.312
Gd	37.8	21.5	54.2	0.261
Pd	190.0	47.9	133	0.384
TaV_2	195	55.5	152	0.370
ZrCr_2	153.5	62.3	165	0.321

Table 1 are for the aggregate elastic moduli. For U, Gd, and Pd, these were calculated from the experimental single-crystal moduli. For the other materials, the experimental values were measured directly for polycrystalline samples. An interesting feature of Table 1 is the rather low Poisson's ratio for U and the rather high value for Pd. There may be some connection of this ratio to the fact that U pulverizes into very fine particles [48] on repeated hydriding/dehydriding while Pd does not. The other materials, with intermediate values of Poisson's ratio, are also intermediate with respect to pulverization.

The connection of elastic properties to thermal properties is made through the Debye theory. The long-wavelength vibrational contribution to the heat capacity at low temperature, T , is given by

$$c_v = \frac{2\pi^2 k_B^4 T^3}{5\hbar^3 v_o^3} = \frac{12\pi^4}{5} \left[\frac{N}{V} \right] k_B \left[\frac{T}{\theta_D} \right]^3 \quad (2)$$

where k_B is Boltzmann's constant. Eq. (2) effectively defines the Debye temperature, θ_D , which is given by

$$\theta_D = \left[6\pi^2 \frac{N}{V} \right]^{1/3} \frac{\hbar}{k_B} v_o \quad (3)$$

where N/V is usually taken [49,50] as the number of atoms per unit volume, and the average sound velocity v_o is given by the expression

$$\frac{1}{v_o^3} = \frac{1}{3} \left[\frac{1}{v_l^3} + \frac{2}{v_t^3} \right] \quad (4)$$

The longitudinal v_l and transverse v_t sound velocities were calculated from the elastic moduli $C_{11} = B + \frac{4}{3}G$, and G , respectively: $v_l = \sqrt{C_{11}/\rho}$ and $v_t = \sqrt{G/\rho}$, where ρ is the density. The values of B and G at 70 K give $v_o = 2.96 \times 10^3$ m/s. The acoustic contribution to the low-temperature specific heat is found to be $C_{ac}/T^3 = 4.70 \text{ J/m}^3 \text{ K}^4 = 9.32 \times 10^{-5} \text{ J/(mol K}^4)$. Similarly, the Debye temperature, calculated from the 3 K moduli, is found to be 347 K. The Debye theory gives an accurate account of the long-wavelength acoustic contribution to the specific heat at low temperatures. Calorimetric measurements, of course, include all contributions, phonon, electronic and any other effects. It appears that there have been no measurements of the low temperature specific heat of ZrCo. If such measurements are carried out, the present work should prove useful in the interpretation of the results.

4. Conclusions

Ultrasonic methods have been used to measure the elastic moduli of the technologically important intermetallic compound ZrCo over the temperature range of 3–410 K. The moduli decrease smoothly with increasing temperature with no indication of a phase change or unusual

electronic effects. Both the magnitude and the temperature dependence of the various moduli, as well as Poisson's ratio, are similar to those of ordinary metals such as copper [40,51]. The acoustic contribution to the low temperature specific heat was also calculated. This calculation should prove useful for a comparison with calorimetric results when such measurements are made. The results should also prove helpful in understanding the elastic energy contributions to the thermodynamics of hydrogen absorption in this system.

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